THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Deaths

WITH deep regret we record the deaths of the following members:

Patrick Henry Kirkaldy, September 14th.
Charles H. La Wall.
Arthur Whitby.

Obituary

FREDERICK WOODLAND TOMS

FREDERICK WOODLAND TOMS, whose death at his home in Jersey on July 20th at the age of 82 was briefly announced in our last number, was the son of Frederick Toms of the editorial staff and, for the latter part of his life, editor-in-chief of *The Field*.

Toms was educated at the City of London School, where he happened to be a contemporary of the writer of these notes, and where a common devotion to the chemical instruction of Henry Durham and Isaac Scarf (still remembered by a few surviving chemical "Old Citizens") led to an intimate friendship which, despite later geographical separation, proved to be lifelong.

On leaving school in 1875 Toms became a pupil assistant of the late R. V. Tuson, Professor of Chemistry at the Royal Veterinary College, where he remained for two years, after which he went for three years to the Royal College of Science, studying chemistry under Professor (later Sir) Edward Frankland, to whom during much of this time he acted as personal assistant chiefly, but not wholly, in matters relating to water analysis. He then went, on Frankland's recommendation, to Dr. (later Sir) William Perkin, in whose organic research laboratory at Sudbury he served for two years.

Following this he went to Guys Hospital as senior assistant in the physiological research laboratory of the late Dr. F. W. Pavy, F.R.S., where he remained until the year 1884, when he was appointed as the first resident Official Analyst to the States of Jersey. The duties of this appointment he carried out for 47 years, retiring in 1931 in favour of his assistant, Mr. C. P. Money, who still holds office.

The Jersey appointment afforded room for considerable activity in connection with the administration of the law relating to adulteration of food, in which, however, Toms for a number of years found himself seriously hampered by the futility of the local application of the milk standards or limits elsewhere in force (or in use), having regard to the natural richness of the milk of Jersey cattle which constitute the only breed on the Island. Ultimately, he was successful in obtaining the official adoption of a local standard more effective for the prevention of adulteration.

Food and drug analysis, however, formed but one phase of his work. His father's connection with agricultural journalism, together with his own early experience at the Veterinary College, had naturally led him to take an interest in such branches of science as bore upon agricultural practice, and he had already contributed to *The Field* a series of articles on the chemistry of ensilage at the time when its novel introduction into farm practice was engaging much attention at home and abroad. He now found under the auspices of the Jersey Royal Agricultural Society ample scope for investigation relating to soils and fertilisers under the intensive system of farming and market gardening prevailing in the Island; and of this he was not slow to avail himself. The consumption of artificial fertilisers in Jersey was then, as it still is, very large in relation to the area of ground under cultivation, and Toms found that at that time local knowledge of the origin, composition and properties of fertilisers was often vague and their use empirical and often illogical, while the prices paid for them were sometimes in anything but reasonable adjustment to their relative intrinsic or productive value.

Toms initiated field experiments on the manuring of the staple crops of the Island, mainly potatoes and tomatoes, in various districts, and the lessons derived from them were promulgated with a clearness and simplicity of exposition which soon led to a confident demand for his advice, as well as to insistence on proper guarantees of composition by the vendors of fertilisers and on the checking of these by analysis. Later such guarantees became legally compulsory, as in this country.

His attention as States Analyst was also demanded in relation to water supplies, gas, building materials and articles coming under fiscal supervision and in other miscellaneous directions.

His experiences in Jersey were mainly recorded in his long series of annual reports, the only paper which he contributed to THE ANALYST being one by himself and C. P. Money on the "Separation of Lead Tetra-Ethyl from Solution in Petroleum Spirit" (ANALYST, 1928, **53**, 328), based upon observations made by Frankland and Lawrence (*J. Chem. Soc.*, 1879, **35**, 244) at the time when he, Toms, was a research student in Frankland's laboratory. The reagent used for the separation of the lead tetra-ethyl was sulphur dioxide and the lead assessment was made by conversion of the reaction product into lead sulphate by "wet combustion."

As an instance of his earlier versatility it may be mentioned that as long ago as 1878 he carried out for *The Field* an investigation into the comparative composition of various explosives used for sporting purposes, finding that the excessive violence of certain brands of wood powder which had been productive of trouble was due to faulty proportion between two varieties of nitrocellulose used

in its composition. A summary of this investigation appeared among the "Abstracts" in the *Journal of the Chemical Society* for 1878 (page 923).

Toms was elected a Fellow of the Chemical Society in 1877 and an Associate of the Institute of Chemistry at the time of its formation in 1878, becoming a Fellow in 1883. He was an original member of the Society of Chemical Industry, and joined the Society of Public Analysts in 1884 at the time of his Jersey appointment.

He was married in 1887 to Emily, daughter of the late Frazer Hopwood, of the Orange Free State, and step-daughter of the late George Snell, of Jersey, who survives him with two sons, one of whom, Frazer Toms, has recently retired from the post of Deputy Inspector-General of Police in the Punjab, while the other, Humphrey Toms, is in medical practice in England.

The life of Toms was one of enthusiastic and unflagging devotion to duty, and his friendship was precious to those who were fortunate enough to enjoy it.

BERNARD DYER

A New Iodine Method for the Determination of Starch. Part IV.

The Determination of Dextrin in the Presence of Starch and Sugars.

BY F. W. EDWARDS, F.I.C., H. R. NANJI, PH.D., D.I.C., F.I.C., AND W. R. CHANMUGAM, F.I.C.

THE name dextrin has been given to many different substances prepared in various ways from starch and starch-containing materials and intermediate in properties between starch and maltose, so that their actual composition is not easy to define. Several varieties exist, all being apparently formed by the breaking down of the complex starch molecule by hydrolysis with acids or enzymes, or by heat. Unfortunately, the name has also been somewhat loosely applied in recent years to degradation products of other higher carbohydrates, such as cellulose and glycogen, and to some products obtained from certain simple carbohydrates by a kind of reversion process. These, however, are more in the nature of research curiosities at the present time, and a very comprehensive account of them is given in Abderhalden's *Biochemisches Handlexikon*.[1] In this communication we are concerned solely with products derived from starch, as these are the only types which are now used at all extensively in many different branches of industry.

In commerce the word "dextrin" is so broadly used that it actually gives little indication of the composition of the products marketed. In the main, these commercial products are mixtures of unaltered starch, dextrin and the reducing sugars dextrose and maltose in varying quantities. The amount of unaltered starch in such dextrins is of some importance. For many industrial uses it should be absent; if present in any material amount it renders the product undesirable, if not unfit, for most of the purposes to which a pure and properly made dextrin is applied. On the other hand, the formation of reducing sugars during manufacture

should also be limited as far as possible, as their presence affects the adhesive and other properties and increases the tendency of the product to be unduly hygroscopic.

It should be clear that the three important determinations, apart from physical determinations such as viscosity, for gauging the value of a sample of dextrin or any other product prepared by partial conversion of starch are: (*a*) true dextrin, (*b*) unconverted starch, and (*c*) reducing sugars.

For estimating dextrin in the presence of starch, Lamb and Harvey[2] determined the cold water extract and used this as a measure of the amount of dextrin, after correcting for sugar and water-soluble ash. Babington, Tingle and Watson[3] regarded this method as not entirely satisfactory because the separation of dextrin from starch by washing with cold water is very difficult, filtration is very slow, and the starch passes into solution during the process to a serious extent. Moreover, the amount of starch indicated includes only insoluble starch, whilst soluble starch is determined as part of the dextrin. They suggested a method of separation in which the starch is precipitated with half-saturated cold solution of barium hydroxide and the dextrin is determined in the filtrate by evaporating an aliquot portion to dryness with sand to constant weight, igniting the residue, and taking the difference in weight before and after ignition to represent the dextrin. These authors admit that starch is not completely precipitated by barium hydroxide, and again no *direct* determination of starch is possible by this method, its amount being obtained by deducting moisture, ash and dextrin from the total weight. In this procedure it is obvious that soluble sugars, which are nearly always present, are included in the dextrin figure.

We have found that it is possible to determine dextrin in presence of starch and sugars by a slight modification of the gravimetric iodine method of Chinoy, Edwards and Nanji[4] for the determination of starch. In that communication it was shown that starch can be precipitated quantitatively as the so-called starch iodide by 95 per cent. alcohol, by a solution of potassium acetate and by other coagulating agents. We have now observed that starch can be precipitated quantitatively as starch iodide from mixed solutions of starch and dextrin, by a mixture of alcohol and potassium acetate, whereas the dextrin is not precipitated at all. The reagent is prepared by adding 4 ml. of 10 per cent. potassium acetate solution to 100 ml. of alcohol (50 per cent. by volume). Precipitation with this reagent also enables a complete separation of soluble starch from dextrin to be made. The starch iodide can be filtered off, washed, dried and weighed, and then a direct determination of dextrin in the filtrate can be made. Full experimental details are given later.

Determination of Dextrin in Presence of Starch.—It was pointed out in the communication mentioned[4] that the gelatinisation of starch by water was unsatisfactory, and we therefore had to use 0·7 per cent. potassium hydroxide solution to obtain satisfactory results. When, however, a mixture of starch and dextrin was gelatinised with 0·7 per cent. potassium hydroxide solution, we consistently obtained low results for dextrin, the amount recovered never exceeding about 80 per cent. of that present, although we tried several different conditions, such as concentration before precipitation, different coagulating agents and so on.

This was unfortunate, since it necessitated two separate determinations, one with water gelatinisation to determine dextrin and the other with alkali gelatinisation to determine starch.

The method finally adopted was as follows:—The mixture of dextrin and starch (not exceeding 1 g.) is made into a paste with about 5 ml. of water in a beaker and about 100 ml. of hot water are gradually added, with stirring. The mixture is allowed to simmer gently for half-an-hour and transferred while hot to a 200-ml. measuring flask, and the beaker is rinsed with further small quantities of water. The mixture is cooled and diluted to 200 ml.

Twenty ml. of the liquid are treated in a 100-ml. measuring flask with 2 ml. of 0·1 *N* iodine solution, and the liquid is made up to 100 ml. with the alcohol and potassium acetate mixture (p. 698), shaken and left for 5 minutes. It is then filtered through an ordinary filter-funnel, and exactly 50 ml. of the filtrate (*i.e.* 10 ml. of the original solution) are evaporated to a small bulk—about 3 to 4 ml. The liquid is then cooled, 100 ml. of 95 per cent. alcohol are added, with stirring, to precipitate the dextrin, and the flask is allowed to stand overnight. The precipitate is filtered off on a tared alundum crucible,* washed with 95 per cent. alcohol, dried and weighed.

Three separate artificial mixtures of starch and dextrin were prepared with 0·5 g. of pure dry maize starch and 0·5 g. of three different samples of pure dextrin. In these dextrin samples the percentage of dry dextrin, as found by precipitation with alcohol, was 88 per cent. in dextrin A, 88 per cent. in dextrin B, and 76 per cent. in dextrin C. The results obtained with the mixtures are given in Table I.

TABLE I

	Dextrin found in 10 ml. g.	Total dry dextrin found g.	Total dry dextrin present g.
Dextrin A	0·021	0·42	
,, ...	0·022	0·44	0·44
,, ...	0·022	0·44	
Dextrin B ..	0·020	0·40	0·44
,, ...	0·020	0·40	
Dextrin C	0·020	0·40	0·38
,, ...	0·021	0·42	

DETERMINATION OF STARCH IN PRESENCE OF DEXTRIN.—The mixture of starch and dextrin (not exceeding 1 g.) is gelatinised with 0·7 per cent. potassium hydroxide solution, cooled and diluted to 200 ml. Ten ml. (or an aliquot portion) are neutralised to phenolphthalein with dilute acetic acid, 1 ml. of 0·1 *N* iodine solution is added, followed by 40 ml. of the alcohol and potassium acetate mixture, and the mixture is left for 10 minutes. The bulk of the liquid is decanted into a tared alundum crucible, the precipitate is washed in the beaker twice with 50 per cent. alcohol and twice with 95 per cent. alcohol, and the precipitate is transferred to the crucible, washed with a little more alcohol, dried and weighed.

* These crucibles are sold in four varieties: dense, medium, coarse and extra coarse, and the only one suitable for the determination of both starch and dextrin is the medium variety.

In Table II are recorded results obtained with two mixtures. No 1 contained 0·25 g. of dextrin and 0·5 g. of pure dry maize starch, and No. 2 contained 0·5 g. of dextrin and 0·5 g. of pure dry maize starch, in 200 ml.; the quantity taken for each determination was 10 ml.

TABLE II

	Weight of starch iodide (10 ml.) (A) g.	Weight of starch found in 10 ml. (A × 0·8865) g.	Weight of starch taken g.
Mixture 1	0·027	0·0239	
,, ...	0·028	0·0248	0·025
,, ...	0·027	0·0239	
Mixture 2	0·028	0·0248	
,, ...	0·029	0·0257	0·025
,, ...	0·029	0·0257	

DETERMINATION OF SUGARS IN DEXTRIN.—The nature of the sugars in dextrin depends on the method of manufacture. If the dextrin is prepared by acid hydrolysis, dextrose is generally present together with a trace of maltose, but if it is prepared by enzyme hydrolysis, maltose is present. It is very difficult to remove the sugars from dextrin, and even in the so-called pure dextrins appreciable amounts of sugar remain.

For the determination of these sugars in dextrin we have found the iodimetric chloramine-T method[5] to give reliable results.

Five to ten ml. of a 1 per cent. solution of dextrin are diluted with 50 ml. of water, and 1 ml. of 0·1 *N* potassium hydroxide solution is added, followed by 2 ml. of 10-per cent. potassium iodide solution and 10 ml. of chloramine-T solution (7·1 g. per litre). After 90 minutes the reaction mixture is acidified with dilute sulphuric acid and the liberated iodine is titrated with 0·02 *N* sodium thiosulphate solution. A blank determination is made under exactly the same conditions as the test, 10 ml. of water being used:

1·4100 g. of iodine ≡ 1 g. of dextrose; 1 ml. of 0·02 *N* iodine ≡ 1·8002 mg. of dextrose
0·7426 g. ,, ,, ≡ 1 g. of maltose; 1 ml. ,, ,, ,, ≡ 3·148 mg. of maltose

The results in Table III show the amount of sugars found in some so-called pure dextrins.

TABLE III

	0·02 *N* iodine consumed ml.	Reducing sugar as dextrose Per Cent.
Weight of dextrin A taken		
50 mg.	1·1	3·96
100 ,, ...	2·25	4·05
Weight of dextrin B taken		
50 mg.	1·8	6·49
100 ,, ...	3·5	6·30
Weight of dextrin C taken		
50 mg.	2·0	7·2
100 ,, ...	4·0	7·2

In order to check the reliability of the chloramine-T method, known quantities of dextrose and maltose were added to different dextrins whose iodine equivalents of the sugars present were already known from the last table, and the total sugars were then determined. In series A (Tables IV and V), 10 ml. of a 1 per cent. solution of dextrin A (containing reducing sugar ≡ 0·45 ml. of 0·1 *N* iodine solution) and varying quantities of dextrose or maltose were taken. In each instance total sugars were determined by diluting to 50 ml., adding 3 ml. of 0·1 *N* potassium hydroxide solution, 10 ml. of 10 per cent. potassium iodide solution and 50 ml. of chloramine-T solution and completing as before. Similarly, in series B, 10 ml. of a 1 per cent. solution of dextrin B (containing reducing sugar ≡ 0·7 ml. of 0·1 *N* iodine solution), and in series C, 10 ml. of a 1 per cent. solution of dextrin C (containing reducing sugar ≡ 0·8 ml. 0·1 of *N* iodine solution) were mixed with different quantities of sugars, and the total sugars were determined as before. Tables IV and V give results obtained with added dextrose and maltose, respectively.

TABLE IV

	Dextrose added mg.	0·1 *N* iodine consumed ml.	Net 0·1 *N* iodine ml.	Dextrose found mg.
Series A ..	19·04	2·6	2·15	19·3
	47·60	5·75	5·3	47·7
Series B ..	19·04	2·8	2·1	18·9
	38·1	4·9	4·2	37·8
	57·1	6·95	6·25	56·3
Series C ..	19·04	2·9	2·1	18·9
	38·1	5·1	4·3	38·7
	57·1	7·1	6·3	56·7

TABLE V

	Maltose added mg.	0·1 *N* iodine consumed ml.	Net 0·1 *N* iodine ml.	Maltose found mg.
Series A ..	18·0	1·55	1·10	18·8
	45·0	3·05	2·60	44·5
	90·0	5·6	5·15	88·0
Series B ..	18·0	1·8	1·10	18·8
	36·0	2·85	2·15	36·7
	54·0	3·75	3·05	52·2
Series C ..	18·0	2·0	1·2	20·5
	36·0	2·95	2·15	36·7
	54·0	3·9	3·1	53·0

We have examined a few samples of commercial dextrins on the lines discussed in this communication, and the results are given in Table VI. They illustrate clearly what enormous variations are possible.

TABLE VI

	No. 1 Per Cent.	No. 2 Per Cent.	No. 3 Per Cent.	No. 4 Per Cent.
Moisture	13·7	10·86	14·8	10·5
Ash	0·24	0·37	0·25	0·13
True dextrin ..	42·0	76·0	12·0	84·0
Starch	42·6	10·0	69·2	1·59
Sugars as dextrose..	0·8	2·4	4·6	1·88

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The Determination of Minute Quantities of Gold in Urine

BY A. R. JAMIESON, B.Sc., F.I.C., AND R. S. WATSON, A.I.C.

(*Read at the Meeting of the Scottish Section, April* **14**, **1938**)

IN THE ANALYST (1937, **62**, 597) Pollard describes a new method for the determination of minute quantities of gold, and states that it can be applied to the determination of gold in the urine of patients undergoing treatment with gold salts. He shows that the method gives excellent results for the recovery of known amounts of gold from solution in tap water, but he gives no figures for the recovery of gold from urine.

To test the accuracy of the process when applied to urine, known amounts of gold solution were added to urine and subsequently determined. The results for the recovery of the gold were at first unsatisfactory and certain modifications described below were introduced. It was found that this modified form of Pollard's process gave very good results when applied to urine.

PRECIPITATION OF GOLD AND TELLURIUM FROM URINE BY SULPHUR DIOXIDE.—When precipitation was carried out by the method recommended by Pollard filtration was unsatisfactory, owing to the finely-divided gold and tellurium passing through the filter, even if a Swedish paper, No. 1 F, and an ordinary filter-funnel were used in place of a Buchner funnel. The filtrate was very dark in colour, and it was practically impossible to ascertain if filtration was satisfactory. In addition, the amount of gold recovered did not correspond with the amount added, especially when the quantities of gold were very small. To overcome these difficulties and increase the size of the particles of the precipitated gold and tellurium, the following modifications were investigated:—(1) addition of common salt to increase the concentration of electrolyte; (2) warming the solution containing the gold and tellurium before precipitation with sulphur dioxide; (3) addition of sodium hydrogen sulphite in place of sulphur dioxide for precipitation.

The most satisfactory method of precipitation was a combination of the first two, *i.e.* by the use of heat and the addition of 7 per cent. of sodium chloride. After standing overnight at ordinary temperature the mixture was heated to boiling, allowed to cool, and then filtered. In this way a clear filtrate was obtained and the recovery of gold was almost complete.

With certain urines it may be possible to dispense with the addition of salt, but it is essential to heat the mixture to boiling after standing overnight if a satisfactory filtrate is to be obtained.

STRENGTH OF STANDARD HYDROQUINONE SOLUTION.—For titration Pollard uses a solution containing 0·4186 g. of pure hydroquinone made up to 500 ml. and runs in this solution from a micro-burette graduated in hundredths of a ml. (1 ml. ≡ 1 mg. of gold). For quantities of 0·1 to 1·0 mg. of gold this gives an exceedingly small titration figure, and attempts were made to use a more dilute solution of the standard hydroquinone solution. It was found that a satisfactory end-point could be obtained by using a solution containing 20 ml. of the strong solution made up to 500 ml. with water; 1 ml. of this solution is equivalent to 0·04 mg. of gold.

USE OF ACID POTASSIUM FLUORIDE AS A BUFFER.—The strength of acid potassium fluoride solution necessary to act as a buffer was not given by Pollard in his original paper. In our experiments it was found that 0·5 ml. of a 5 per cent. solution of acid potassium fluoride in 50 ml. of solution containing the gold gave satisfactory results. Any further increase in the amount of fluoride had no appreciable effect on the sharpness of the end-point.

SUGGESTED MODIFICATION OF POLLARD'S METHOD WHEN USED FOR THE DETERMINATION OF GOLD IN URINE.—Take 500 ml. of urine, add 50 ml. of conc. hydrochloric acid, 0·1 ml. of tellurium solution* (of which 1 ml. contains 100 mg. of tellurium) and 35 g. of sodium chloride. Warm slightly and pass sulphur dioxide through the solution until it is saturated and has a strong odour of sulphur dioxide. Leave overnight, heat to boiling-point, cool, and filter through a Swedish filter-paper No. 1 F. Wash the residue twice with cold water, transfer the filter-paper and precipitate to a small crucible, dry, and ignite to burn off the tellurium. Dissolve the residue of gold in *aqua regia* (2 drops of conc. nitric acid and 6 drops of conc. hydrochloric acid), assisting solution by placing the crucible on the top of the water-bath for 15 minutes, as recommended by Pollard. Then place the crucible in the apparatus shown in the diagram and allow a current of air to impinge on the surface of the liquid in the crucible to remove excess of chlorine and nitrosyl chloride.

Wash the contents of the crucible into a Nessler tube and make up to 50 ml. with water. Add 0·5 ml. of 5 per cent. acid potassium fluoride solution and 1 ml. of *o*-dianisidine solution (0·5 g. of *o*-dianisidine for 500 ml. of solution containing 2 ml. of conc. hydrochloric acid). Leave for 10 minutes until the colour reaches its full intensity. Titrate with the standard hydroquinone solution (0·0335 g. of hydroquinone per litre; 1 ml. ≡ 0·00004 g. of gold).

The apparatus (see Fig. 1) for the removal of chlorine and nitrosyl chloride by means of a current of air, consists of a suction flask with the base removed and the lower edge ground to fit a ground-glass plate, on which rests the crucible containing the gold solution.†

* Pollard (*loc. cit.*) prepares this solution by dissolving 5 g. of powdered tellurium in 20 ml. of hydrochloric acid and 5 ml. of nitric acid on a water-bath, then removing the nitric acid by evaporating to a thick syrup after addition of hydrochloric acid, and finally adding 25 ml. of hydrochloric acid and making up to 50 ml. with water.—EDITOR.

† This apparatus can be obtained from Messrs. McCulloch Bros. & Wilson, 46A, West Princes Street, Glasgow, C.4.

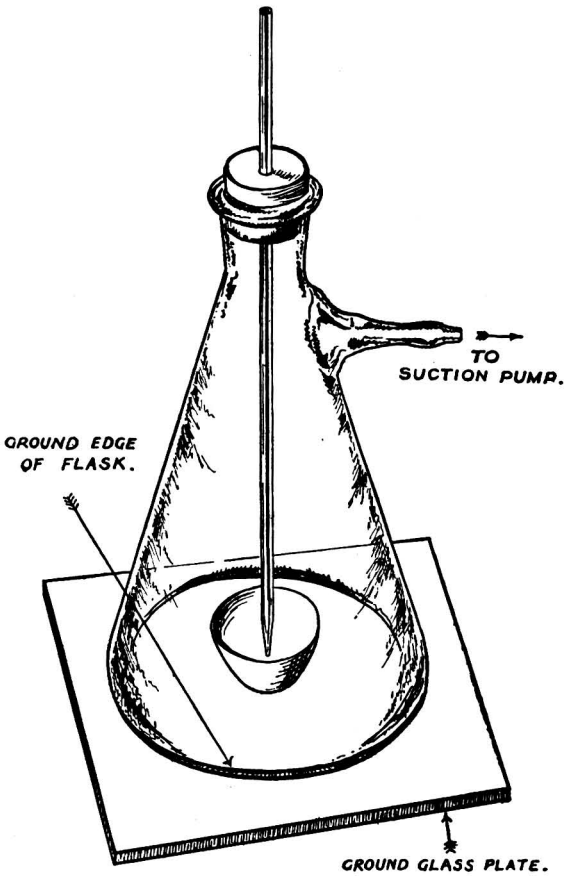

Fig. 1

The results of the analysis of urines containing known amounts of gold were as follows:

Titration, ml. of hydroquinone	1·71	6·56	3·85	8·68	12·39	1·67	2·70	4·85	2·67	3·17
Gold added, mg. ..	0·085	0·262	0·174	0·348	0·522	0·087	0·131	0·218	0·113	0·150
Gold found, mg. ..	0·068	0·256	0·154	0·347	0·496	0·067	0·108	0·194	0·107	0·127

Blank determinations on the reagents gave negative results.

We are indebted to Mr. T. Cockburn, F.I.C., for permission to publish the results of this investigation.

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Residual Fat in Solvent-extracted Materials

By H. C. LOCKWOOD, B.Sc., F.I.C.

In 1892 Weibull[1,2,3] observed that the fat in bread could not be completely extracted with solvents to give results agreeing with the fat-content of the flour used. He found, however, that by digesting with boiling sulphuric acid all the fat was liberated from flour or bread and concordant results were obtained. In his method the acid mixture was neutralised with marble, absorbed on blotting-paper and extracted after drying. Weibull's principle has been modified by other workers, such as Neumann[4] and Mohs,[5] in that hydrochloric acid has been used instead of sulphuric acid.

More recently this point has been investigated by Fincke,[6] Janssen,[7] and Fincke and Niemeyer,[8] and their results are of particular interest. Fincke[6] showed that the fat in cacao mass was not completely extracted and he therefore recommended boiling with 4 *N* hydrochloric acid in order to liberate the fat from the cells.

The results and deductions of Janssen[7] are open to considerable criticism. Weighed amounts of cocoa butter and cows' butter were boiled for 15 minutes with 4 *N* hydrochloric acid. The mixtures were filtered, washed and dried, and 100 per cent. recovery was obtained by extraction. The properties of the fats so recovered showed very little change with regard to iodine, saponification and Reichert values and refractive index. Janssen deduces that fats extracted by the modified Weibull method will have suffered no change in physical or chemical properties. An important point overlooked is that the action of hydrochloric acid on the comparatively large fat-globules of cocoa butter would almost certainly be less than its action on the minute particles of fat during their liberation from cacao materials.

Janssen tested a known mixture of sugar, cocoa butter and dry fat-free cocoa. With the modified Weibull method he realised 100 per cent. recovery, but it would be interesting to know how he obtained "du cacao complètement dégraissé." It is obvious that any retained fat in the virtually fat-free cocoa would increase the possibility of 100 per cent. recovery, so that Janssen should have obtained a slight increase in fat over the amount added. Reference to Table I shows that cocoa material thoroughly extracted with solvents still contains sufficient fat to influence a test of the above nature. Janssen generally records his fat percentages to the third place of decimals. The results of my work indicate that such accuracy cannot possibly be attained by the methods employed, and that a considerable advance will have been made when different workers agree as to the fat-content in cacao products to within 0·1 per cent.

Fincke and Niemeyer[8] compared several methods available for the determination of fat in cacao products. With the exception of those obtained by Weibull's principle, their highest results were generally those by the centrifuge method; the Soxhlet process was not applied, presumably owing to the objection to hot extraction. They obtained an appreciable increase in fat when the modified Weibull method was applied, using ethyl ether as solvent. With petroleum spirit an increase was generally shown, but it is hardly to be expected that the results would

agree closely with those obtained by the use of ethyl ether—a solvent very liable to extract substances other than fat.

In my experience[9] the technique was unsatisfactory when applied to cacao products containing high percentages of fat. The method was applied to solvent-extracted materials, and the preliminary results showed that further investigation was required.

AIM OF THE INVESTIGATION.—The main object of this research was to find what effect the state of division had on the fat-content of food products which had been extracted as thoroughly as possible with hot petroleum spirit. It was decided to separate each material into three grades by the use of sieves, and this was done whenever the original state of the substance permitted. The sieves selected were of the woven silk variety and were numbered 5, 10 and 25, these being equivalent to British Standard sieves 60, 120 and 200, respectively. The three fractions are therefore designated "5–10," "10–25," and "through 25," and the approximate dimensions of the particles were 0·15 to 0·25 mm., 0·075 to 0·15 mm., and up to 0·075 mm., respectively.

PREPARATION OF SAMPLES.—The materials were first sieved completely through the No. 5 silk. With powders this was readily accomplished, but fatty materials, such as cacao mass, were partly de-fatted by boiling with petroleum spirit (b.p. 60°–80° C.), filtering on a Buchner funnel and drying. The materials were then sieved on the No. 10 silk and the fine particles again on the No. 25. The three fractions were extracted for 20 hours in Soxhlet extractors with the petroleum spirit. The residues, generally weighing 3 to 4 g., were refluxed with 100 ml. of petroleum spirit, and the extracts were filtered and evaporated. With most substances the fat thus obtained from the residues did not exceed 1 or 2 mg., and, if so, the materials were considered to be thoroughly extracted. The residues from the "5–10" fractions of cacao mass and biscuits, however, yielded appreciable amounts of fat, and the three grades of those materials were therefore again extracted for 20 hours.

The de-fatting and consequent handling were found to have a disintegrating effect on the coarser particles. The dry "fat-free" materials of the "5–10" and "10–25" grades were sieved again to separate the fine particles, which were added to their respective grades.

DETERMINATION OF RESIDUAL FAT.—Three g. of dry extracted material were transferred to a 150-ml. beaker and 50 ml. of 4 *N* hydrochloric acid were added. The mixture was heated to boiling and allowed to boil gently for 15 minutes, the beaker being covered with a watch-glass. At several intervals during the boiling the contents were stirred with a glass rod to remove material which had settled on the sides of the beaker owing to frothing. The contents were collected on a 12·5-cm. Swedish filter-paper and washed thoroughly with hot water, a total volume of 300 ml. being used. The filter-paper was placed in a flat dish, and the residue was spread out to aid drying. The dried residue was removed from the paper and powdered either in a small glass mortar or on a piece of paper with a small palette knife. The powdered residue was returned to the original filter-paper which was made to form a bag. This was placed inside another filter-paper folded as a thimble and then wired round the middle. The final extraction was

made with petroleum spirit (b.p. 40–60° C.) for 20 hours in the apparatus devised by me.[9] A Soxhlet or any other efficient extractor could be used.

The foregoing procedure was applied to 19 materials, and the results, to two significant figures, are given in Table I.

TABLE I

RESIDUAL FAT IN SOLVENT-EXTRACTED MATERIALS

Expt. No.	Material	Grading "5–10" Per Cent.	Grading "10–25" Per Cent.	Grading "Through 25" Per Cent.
1	Nib, normal roast for cocoa	4·7	2·8	0·57
2	Nib, low roast for chocolate	2·9	1·2	0·50
3	Unroasted cacao nib A	1·8	0·64	0·60
4	,, ,, ,, B	1·3	0·88	0·67
5	Roasted shell	—	0·34	0·30
6	Unroasted shell A	0·43	0·50	0·39
7	,, ,, B	0·33	0·39	0·41
8	Cocoa powder	—	0·95	0·70
9	Plain chocolate	—	—	0·20
10	Unfinished chocolate	—	—	0·12
11	Coarser particles separated from plain chocolate	—	—	0·04
12	Skimmed milk powder	—	1·1	0·97
13	Full-cream milk powder	1·5	1·4	1·1
14	Unfinished milk chocolate	—	0·55	0·55
15	Milk chocolate	—	—	0·57
16	Coarser particles separated from milk chocolate	—	—	0·47
17	Biscuit flour	—	0·44	0·30
18	Biscuits	0·90	0·77	0·47
19	Coffee (roasted)	1·4	0·82	0·37

Reference to the results in Table I shows several points of interest. Possibly the most important is that grades "5–10" and "10–25" of roasted nib retain considerably more fat than corresponding grades of unroasted nib. In addition, the higher the roast the less completely was the fat extracted from the two coarser grades. The beans used for Expts. 1 to 7 were all grown on the West Coast of Africa. The results on cacao shell are rather erratic, but it is doubtful if the hydrochloric acid fully attacks the larger particles. To confirm this opinion No. 7 was ground with sand after the quantitative extraction and again extracted; a further 0·23 per cent. of fat was obtained from the "5–10" grade. The same grade of nib after similar treatment gave an additional 0·25 per cent., but no more fat was obtained from biscuits or dried milk powder.

It will be noted that skimmed and full-cream milk powders gave results of the same order, and the particle-size, although making some difference, was not of outstanding influence. Finished and partly finished milk chocolate showed a practically constant result of 0·55 per cent., which is in accordance with the parallel character of results obtained with milk powders.

Expts. 11 and 16 were concerned with the coarser particles separated from plain and milk chocolate. The materials were obtained by repeated sedimentation

from petroleum spirit, and the residual-fat percentages are lower, owing to the preponderance of sugar in this type of material.

Effect on Fat Percentage in Original Material.—The results in Table I show that the fat percentage of the original material will be affected according to the total fat-content and state of division. Cacao nib contains approximately 55 per cent. of cocoa butter, and treatment with hydrochloric acid will give an increase of at least 0·3 per cent. in the very finely-ground product. Treatment of cacao shell with hydrochloric acid will enhance the result by 0·3 to 0·4 per cent., whilst on cocoa powder containing 25 per cent. of fat the increase would be approximately 0·6 per cent. Other calculated results, applicable to finely-ground materials, are given in Table II.

Table II

Material	Approximate amount of fat extracted with petroleum spirit Per Cent.	Increase by HCl treatment Per Cent.
Cacao nib	55	>0·3
Cacao shell	4	0·3 to 0·4
Cocoa powder	25	0·6
Plain chocolate	33	0·15
Skimmed milk powder ..	0·1	1·0
Full-cream milk powder ..	25	1·0
Milk chocolate	33	0·3 to 0·4

Melting-points of Extracted Residual-Fats.—The residual fat, extracted after treatment with hydrochloric acid, was allowed to remain at room temperature for 6 to 7 days. The m.p. was then determined, according to the technique of Knapp,[10] by placing scrapings on the bulb of the thermometer, which was then inserted in a test-tube and gradually warmed in a beaker of water. Usually the extracted fats had rancid odours, and too much importance should not be attached to the readings given in Table III.

Reference to the results in Table III shows a marked parallelism between the three grades in Expts. 1 and 2, and also between those in Expts. 3 and 4. It is interesting that cocoa powder, plain chocolate and unfinished chocolate give melting-points ranging from 37° to 40° C., whereas cocoa butter melts at 32° C.—the temperature which should be borne in mind when considering the results in Expts. 1–10 inclusive. Expts. 12–16, dealing with dried milk and milk chocolate, show fairly uniform results, and the melting-points range from 28° to 32° C.

Conclusions and Summary.—The modified Weibull's method has been applied to cacao and other products which have been thoroughly extracted with hot petroleum spirit. The results show that appreciable amounts of fat-like substances are retained and that the quantity increases with the particle-size, but to a much greater extent with cacao mass than with dried milk or milk chocolate. From the melting-points of the residual fats it appears that the substances extracted after treatment with hydrochloric acid are not identical with the bulk of the fat originally present, and for this reason should be kept separate if the fat is to be analysed subsequently.

The modified Weibull method, applied by other workers to the original materials, has been found unsatisfactory,[9] particularly with regard to the manipulation required, and it is recommended that the finely-ground substance should be thoroughly extracted with hot petroleum spirit in an efficient extractor. The residue should be dried, treated with hydrochloric acid, washed and dried. If the main bulk of the fat is required for analysis, the residual fat should be extracted and collected in a separate flask.

TABLE III

MELTING-POINTS OF RESIDUAL FATS

Expt. No.	Material	Grading "5–10" °C.	Grading "10–25" °C.	Grading "Through 25" °C.
1	Nib—normal roast for cocoa ..	29	29	39
2	Nib—low roast for chocolate ..	30	30	40
3	Unroasted cacao nib A	31	37	39
4	,, ,, ,, B	32	37	39
5	Roasted shell..	—	49	47
6	Unroasted shell A	36	39	41
7	,, ,, B	50	54	45
8	Cocoa powder	—	37	37
9	Plain chocolate	—	—	40
10	Unfinished chocolate	—	—	39
11	—			
12	Skimmed milk powder	—	32	31
13	Full-cream milk powder	28	29	28
14	Unfinished milk chocolate	—	30	30
15	Milk chocolate	—	—	30
16	Coarser particles separated from milk chocolate	—	—	29
17	Biscuit flour	—	48	45
18	Biscuits	26	26	25
19	Coffee (roasted)	16*	20	27

* Allowed to set at 0° C.

For routine work applying to factory control the extra manipulation is scarcely justified, especially when suitable corrections could be applied to finely-ground materials. The approximate adjustments would be 0·1 per cent. for plain chocolate, 0·3 per cent. for cacao mass, cacao shell and milk chocolate, and 0·6 per cent. for cocoa powder, but before final recommendations could be proposed considerably more determinations would have to be made. For skimmed or full-cream milk powders, in which the residual fat amounts to 1 per cent., the process of the Milk Products Sub-Committee[11] should be used; their method is based on the work of Werner–Schmid,[12] Rose,[13] and Gottlieb.[14]

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The Chromium Compound of 8-Hydroxyquinoline

BY E. TAYLOR-AUSTIN, A.I.C.

IN the literature so far published on the use of 8-hydroxyquinoline or oxine in quantitative analysis, little or no mention is made of the behaviour of the element chromium. During a recent investigation on the application of oxine to the determination of aluminium in cast iron,[1] it was found that the presence of chromium causes interference by contamination of the aluminium oxine complex. A further investigation was therefore carried out with a view to establishing the behaviour of chromium under various precipitation conditions and the composition of its oxine complex.

Generally speaking, there are four methods of precipitation in use at the present time for determinations by means of oxine:—(*a*) in acetic acid and acetate solutions containing ammonium acetate[1,2]; (*b*) in hydrochloric acid solutions containing ammonium chloride[1,3]; (*c*) in sodium hydroxide solutions containing either sodium or ammonium acetate[4]; (*d*) in ammonium hydroxide solutions.[5]

Referring to these procedures, it should be noted that so far as aluminium is concerned, conditions of precipitation (*b*) are only applicable to small amounts (1 to 2 mg.), but that whereas in conditions (*a*) manganese is partially precipitated by oxine, in (*b*) there is no interference by this element.

Although chromium yields precipitates under all the above-mentioned conditions whether it is present as a chromic salt or as a chromate, only in sodium hydroxide and ammonium acetate solution does its precipitation approach completion. The amount precipitated in acetic acid and acetate or hydrochloric acid and ammonium chloride solutions appears to depend upon the amount of aluminium present. If aluminium is absent no precipitate is obtained in the latter method (HCl–NH_4Cl), but in acetic acid and acetate solution a small precipitate is obtained on boiling. In both methods, the more nearly the ratio of chromium to aluminium approaches 1 : 1, the greater is the contamination due to chromium. Thus with 0·75 per cent. of chromium and 7 to 8 per cent. of aluminium the interference is negligible for routine purposes, but with 0·75 per cent. of chromium and 1·0 per cent. of aluminium approximately 0·5 per cent. of chromium is precipitated with the aluminium in acetic acid and acetate solution. Similarly, in hydrochloric acid and ammonium chloride solution with 0·0010 g. of aluminium and 0·002 g. of

chromium, approximately 50 per cent. of the chromium present is precipitated, but with 0·001 g. of aluminium and 0·0010 g. of chromium, the whole of the chromium and aluminium are precipitated together.

In view of the fact that the metallic complexes of oxine contain only a small amount of the metal, it was deemed unnecessary to employ solutions containing large amounts of chromium. Accordingly, solutions containing 10 mg. of chromium were used for the investigation. The chromium solution used was made up as follows: 0·5654 g. of potassium dichromate (AnalaR) was dissolved in 200 ml. of water, and the chromium was reduced to the tervalent state by adding sulphurous acid and expelling the excess of sulphur dioxide by boiling. The solution was diluted to 1 litre, with its acidity adjusted to 1 per cent. of sulphuric acid; 50 ml. of this solution contain theoretically 10 mg. of chromium. The exact amount of chromium in the solution was not determined, since after all the precipitations the filtrates were examined for unprecipitated chromium.

The conditions found to give the maximum yield of the complex were as follows:—To 10 ml. of the solution containing the chromium add ammonium hydroxide until a faint permanent precipitate appears, just re-dissolve this with sulphuric acid, and warm to a temperature of 70° C. Next add 20 ml. of a 2 per cent. solution of oxine in acetic acid,* followed by 20 ml. of *N* sodium hydroxide solution and 20 ml. of 4 *N* ammonium acetate solution. No immediate precipitation takes place, but this begins on warming again to 70° C. Boil the solution for one minute (precipitate coagulates), filter hot on a weighed sintered glass crucible (No. 4 porosity), and wash six times with boiling water. Dry the crucible and its contents to constant weight at 105° to 110° C.

The results obtained by this method are given in Table I, and it will be seen from the amount of chromium remaining in the filtrate that under these conditions 99·0 per cent. of the chromium present is precipitated.

TABLE I

Expt. No.	Chromium added g.	Weight of oxine complex g.	Chromium in complex Per Cent.	Oxine in in complex Per Cent.	Chromium in filtrate g.	Total chromium found g.
1	0·0100	0·0915	10·745	—	0·00017	0·00991
2	0·0100	0·0910	10·743	88·83	0·00014	0·00992
3	0·0100	0·0908	10·760	89·08	0·00014	0·00982
4	0·0100	0·0909	10·761	88·96	0·00017	0·00993
5	0·0100	0·0906	10·754	88·65	0·00021	0·00995
6	0·0100	0·0904	10·748	88·72	0·00020	0·00993
7	0·0100	0·0908	10·754	88·70	0·00012	0·00987
8	0·0100	0·0910	10·740	88·77	0·00010	0·00988
9	0·0100	0·0909	10·747	88·67	0·00015	0·00991
10	0·0100	0·0908	10·744	88·94	0·00016	0·00991

The chromium oxine complex was dissolved from the filter after weighing, and chromium and oxine were determined—the chromium by titration with ferrous ammonium sulphate and potassium permanganate and also by precipitation with ammonium hydroxide after the destruction of organic matter, and the oxine by

* Two per cent. of oxine in 2 *N* acetic acid, as recommended by Mitchell and Ward.[6]

titration with potassium bromate-bromide and sodium thiosulphate.[7] The amount of chromium in the filtrates was determined by the diphenylcarbazide colorimetric method after destruction of the excess of oxine. The results obtained are given in Table I, and it will be seen that they are in close agreement with the theoretical figure of 10·74 per cent. of chromium calculated on the assumption that chromium forms the complex $(C_9H_6ON)_3Cr$.

Further proof of this was obtained by precipitating a known amount of aluminium and chromium together, determining the chromium in the mixed complex, and making a correction on the total weight, based upon the fact that $(C_9H_6ON)_3Cr$ contains 10·74 per cent. of chromium. The corrected figures for aluminium were in agreement with those obtained in the absence of chromium.

Thus it may be concluded that chromium forms a compound with 8-hydroxyquinoline under all the conditions given and that the compound conforms with the formula $(C_9H_6ON)_3Cr$.

I wish to express my thanks to the Director and Council of the British Cast Iron Research Association for permission to publish this work.

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The Rapid Determination of Phosphorus in Mild Steel

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

The alkalimetric phosphomolybdate method for the determination of phosphorus in steel presents two difficulties from the point of view of accuracy and rapidity. First, the precipitation is apt to be incomplete except in hot solution, when, on the other hand, contamination with arsenic occurs. Secondly, the precipitate requires a somewhat tedious thorough washing, to remove all traces of nitric acid, before it may be dissolved in standard alkali. Furthermore, the method depends on securing a constant ratio of phosphorus to molybdenum in the precipitate.

The first difficulty is usually overcome either by precipitation from hot solution followed by one or other of various lengthy processes for the removal of arsenic; or by precipitation from tepid solution and a "standardisation" of the method

by the use of a steel of known phosphorus-content. In the present paper, the second procedure, being much the more rapid, is investigated and shown to be tolerably reliable if exact conditions of procedure are adhered to, and provided that the phosphorus being precipitated is present in amounts not less than about 0·4 mg. per 1 g. of iron.

The second difficulty may be avoided by an adaptation of the colorimetric method originally due to Osmond,[1] who utilised the blue colour of the reduction product formed when the phosphomolybdate is dissolved in acid stannous chloride. His technique was far from ideal and, although the "molybdenum-blue" method for the determination of phosphate has since undergone innumerable modifications[2] in biochemical hands, it has not yet found favour with metallurgists for steel analysis. The method, as improved chiefly by Denigès[3] and Truog and Meyer,[4] is adapted in the present work to the rapid and accurate determination of phosphorus in the phosphomolybdate precipitate, and is thought to be much more convenient than the alkalimetric procedure. Photoelectric colorimetry may be employed with advantage.

In the method described below the steel is dissolved in nitric acid in the usual way, and the oxidation is completed with permanganate, the excess of which is removed with nitrite, as recommended by Etheridge.[5] The phosphomolybdate precipitation is carried out in tepid solution, to avoid co-precipitation of arsenato-molybdate, which also gives a blue reduction product. The roughly-washed precipitate is dissolved in excess of sodium hydroxide solution; the phosphate may then at once be determined by the addition of strongly acid ammonium molybdate and stannous chloride, as in the procedure of Truog and Meyer.[4] A small correction is applied for the phosphorus not precipitated by the molybdate in tepid solution.

SOLUTIONS REQUIRED (in order of use):

(1) 4 *N* Nitric acid. Dilute 254 ml. of conc. nitric acid (sp.gr. 1·42) to 1 litre.

(2) Potassium permanganate solution, 15 g. per litre.

(3) Sodium nitrite solution, 10 g. per litre.

(4) Conc. nitric acid (sp.gr. 1·42).

(5) "Neutral" ammonium molybdate solution.[6] Dissolve 55 g. of ammonium molybdate and 50 g. of ammonium nitrate with 45 ml. of 6 *N* ammonia (sp.gr. 0·90) in about 700 ml. of water, and make up to 1 litre.

(6) Dilute (about 2 per cent.) nitric acid.

(7) Sodium hydroxide solution, 20 g. per litre.

(8) "Acid" ammonium molybdate solution.[4] Dissolve 12·50 g. of ammonium molybdate in 100 ml. of water at 60° C., filtering if necessary. Dilute 140 ml. of conc. sulphuric acid to about 800 ml. When both solutions are cool, add the molybdate slowly, with shaking, to the acid, and make up to 1 litre. The solution is 5 *N* in sulphuric acid.

(9) Stannous chloride solution, 25 g. per litre. Dissolve 25 g. of $SnCl_2.2H_2O$ in 100 ml. of conc. hydrochloric acid, and make up to 1 litre. Store this stock solution under oil or hydrogen.

(10) Diluted stannous chloride solution. Take 10 ml. of stock solution (9) and dilute to 100 ml. This solution keeps for a few hours only.

(11) (For photoelectric colorimetry only.) "Standard blue." Dissolve 2·50 g. of copper sulphate ($CuSO_4.5H_2O$) and 0·147 g. of potassium dichromate in water, add 35 ml. of conc. ammonia (sp.gr. 0·880) and make up to 1 litre. Stopper well.

PROCEDURE.—Dissolve 1·5 g. of the steel in 40 ml. of 4 *N* nitric acid (1) in a 200-ml. conical flask.* Boil to remove nitrous acid (2 minutes) and add a few ml. of potassium permanganate solution (2) to oxidise all phosphorus to phosphate, boiling until manganese dioxide is precipitated (5 minutes). Add just sufficient sodium nitrite solution (3) to give a clear solution and 13 ml. of conc. nitric acid (4). Boil for 2 minutes to remove nitrous acid. Cool to 60° C. and add 50 ml. of "neutral" ammonium molybdate solution (5); the temperature should now be 36°–38° C. Stopper the flask and shake vigorously for 15 minutes, leave for 10 minutes, and filter through a Gooch crucible, washing the precipitate five times with dilute nitric acid (6) and once with water. Replace the filter-flask by a clean one, and pour 5 ml. of sodium hydroxide solution (7), warmed to 70° C., over the precipitate. Wash through the solution with four small amounts of warm water, transfer the cooled filtrate to a measuring flask and make up to 50 ml. Take a 2-ml. aliquot portion in a 50-ml. flask with a mark at 40 ml. Make up to 40 ml., add 4·00 ($\pm$0·02) ml. of "acid" ammonium molybdate solution (8), mixing well, and then 5·0 ($\pm$0·2) ml. of diluted stannous chloride solution (10) and water to 50 ml., mixing rapidly. Leave for 10 minutes (15 minutes in cool weather), and then compare with a simultaneously made standard, or measure the colour on a tintometer or photoelectric colorimeter, using a calibration curve. The quantities stated produce about 0·02 to 0·06 mg. of phosphorus in the 50-ml. flask, which gives a suitable colour for 1-cm. cells. Greater dilution is necessary if a colorimeter with long cells is employed.

For the greatest accuracy, prepare the standard solutions in the same way as for the test solutions described below, containing iron, nitric acid, etc. Precipitate the phosphate as phosphomolybdate, and re-dissolve this in sodium hydroxide solution, just as in the determination. All blank errors and precipitation errors are then automatically eliminated. For routine work, it is permissible to use simple phosphate standards prepared from a suitable dilute solution of potassium di-hydrogen phosphate, since the reagents used throughout the determination can be obtained sufficiently free from phosphate to make the blank error negligible. Under these conditions, however, a correction (*vide infra*) must be made for the precipitation error.

When a tintometer or photoelectric colorimeter is used, set up a calibration curve using solutions of known phosphorus-content. It is convenient to obtain the readings for 0·02, 0·03, 0·04, 0·05, and 0·06 mg. of phosphorus per 50 ml., then to obtain the readings for the unknown solutions, and finally to complete the calibration with the readings for 0·025, etc. mg. of phosphorus per 50 ml. In this

* For steels with P<0·04 per cent., add 0·5 mg. of phosphorus as phosphate at this point. See later.

way changes in conditions during the determination, which should not occur, may be detected. It is advisable to wash out the colorimeter cell with conc. nitric acid after every six or seven determinations, as the blue colour tends to be precipitated very slightly on the glass. Six or seven colorimetric determinations can conveniently be made in one batch, from the point where the 2-ml. aliquot portion is taken, since when the sixth or seventh has been prepared, the first has stood for the requisite 10 minutes.

In photoelectric colorimetry, instead of renewing the fading molybdenum-blue solution in the "standard" cell from time to time, it is better to use the blue solution (11) as an artificial sub-standard. This solution is constant in colour if evaporation is prevented; this may be achieved by cementing a small slip of glass over the cell. The instrument is calibrated in terms of the artificial standard and the various phosphate standards in the ordinary way, the usual electric lamp without a colour filter being used.

INVESTIGATION OF THE METHOD.—(*a*) *Reproducibility of the Molybdenum-Blue Colour.*—Since the points now to be discussed depend on the accuracy of the colorimetric part of the analysis, this matter will be taken first. Fig. 1 shows a typical

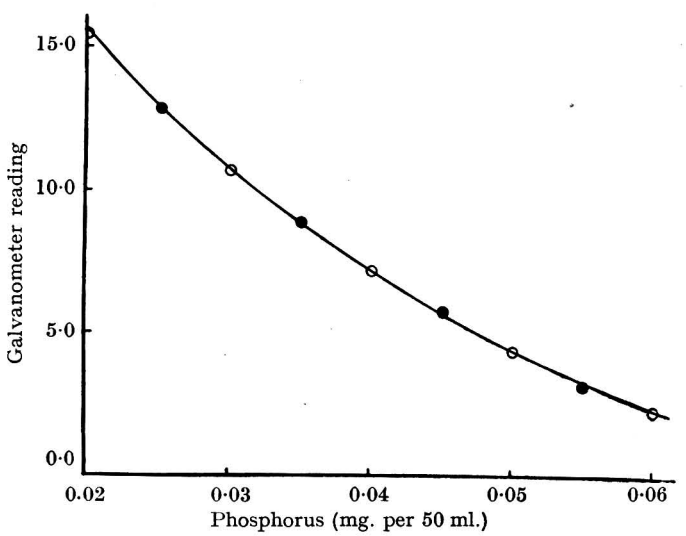

Fig. 1

calibration curve for a photoelectric colorimeter, with solution (11) in the "standard" 1-cm. cell, and the light intensity adjusted to give a deflection of 10·0 galvanometer scale divisions with this cell in the path of the light-beam. The points marked with black circles were obtained about 1 hour after those marked with plain circles, and all the points lie on a smooth curve. Owing to changes in the stannous chloride reagent, calibration curves obtained on different days vary somewhat. However, the curve is quite constant during the time taken for a set of 10 to 20 determinations. This is shown by the figures in Table I, taken at random from numerous curves similar to Fig. 1; the true phosphorus figures for

the "black-circle" points, and that calculated on the assumption that the "plain-circle" points first obtained are correct, agree very closely.

TABLE I

True phosphorus-content mg. per 50 ml.	Calculated phosphorus-content mg. per 50 ml.					
0·0250	0·0255	0·0250	0·0252	0·0250	0·0249	0·0247
0·0350	0·0348	0·0346	0·0348	0·0358	0·0350	0·0350
0·0450	0·0450	0·0450	0·0450	0·0446	0·0457	
0·0550	0·0553	0·0550	0·0546	0·0550	0·0551	

(*b*) *The Precipitation Error.*—Most previous work, notably that of Lundell and Hoffmann,[7] shows that practically all the phosphorus is precipitated as phosphomolybdate at 35° to 40° C. within half-an-hour. The following experiments show that there is a small error, but that this is almost regular, if the conditions are exactly controlled, for amounts of phosphorus between 0·6 and 1·2 mg.

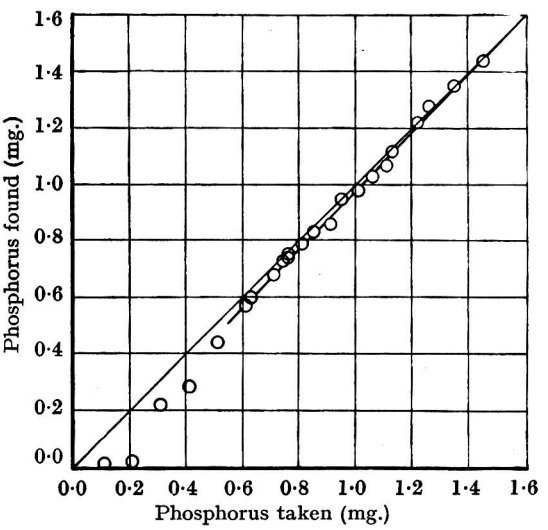

Fig. 2

Test solutions were made up from arsenic-free low-phosphorus "pure" iron, with nitric acid in the standard amounts, and with known additions of phosphate corresponding to the percentages of phosphorus normally found in mild steel. The small amount of phosphorus in the "pure" iron was determined by precipitation as phosphomolybdate from nearly boiling solution, the precipitate being allowed to stand overnight before filtration, and being then treated by the colorimetric method. Duplicate results were 0·001, 0·001 per cent. of phosphorus. The test solutions were analysed for phosphorus by the method as described, from the point where the permanganate is added. All glass measuring apparatus was calibrated. The results are shown in Fig. 2 as a comparison between "phosphorus taken" and "phosphorus found without correction for precipitation error." The best curve

through the experimental points gives, as mean error, —0·03 mg. for 0·6 mg. of phosphorus taken, —0·02 mg. for 0·9 mg., and —0·01 mg. for 1·2 mg. Above about 1·3 mg. of phosphorus the error is negligible.

The precipitation of small amounts of phosphomolybdate, obtained from steels low in phosphorus, is well known to be unreliable at low temperatures. This is confirmed by the irregular nature of the points in Fig. 2 representing the determination of amounts of phosphorus below 0·6 mg. Therefore, in the determination of phosphorus in steels having phosphorus $< 0{\cdot}04$ per cent., 0·5 mg. of phosphorus should be added as phosphate before the precipitation, to bring the phosphate-content into the region where consistent results can be obtained. The phosphate derived from the steel is then obtained by subtraction.

(*c*) *Results of Analyses of Unknown Solutions.*—To test the complete method, including the elimination of the precipitation error by means of the standardisation curve obtained in the previous section, and to investigate any influence of arsenic, further test solutions were analysed by a worker to whom their composition was unknown. The results are given in Table II.

TABLE II

Iron taken g.	Arsenic taken (as arsenate) mg. As	Total phosphorus taken (as phosphate + 0·001 per cent. P in iron) mg. P	Phosphorus found (corrected for precipitation error) mg. P
1·5	0·0	0·84	0·83
1·5	0·0	0·88	0·87
1·5	0·0	1·02	1·03
1·5	1·5	0·80	0·80
1·5	1·5	0·93	0·95
1·5	1·5	1·09	1·09

The accuracy is good. Also, arsenic corresponding with as much as 0·1 per cent. in steel evidently does not interfere, and the traces of iron and acid remaining in the precipitate after the rough washing are unobjectionable.

This work has been carried out for the International Tin Research and Development Council in connection with investigations of the steel-base of tinplate.

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THE METALLURGICAL LABORATORIES
UNIVERSITY OF CAMBRIDGE

March, 1938

Notes

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

A TEST FOR HYDROXYLAMINE AND HYPONITROUS ACID

SEVERAL tests are available for the detection of small amounts of hydroxylamine, such as those of Angeli (*Ber.*, 1896, **29**, 1884), Ball (*Proc. Chem. Soc.*, 1902, **18**, 9) and Blom (*Ber.*, 1926, **59**, 121), but until comparatively recently, so far as we are aware, no sensitive test for the detection of traces of hyponitrous acid had been published. In 1934, Corbet (*Biochem. J.*, 1934, **28**, 1575) described a test depending on the production of an orange or cherry-red colour on adding resorcinol and potassium periodate to a neutral solution of a hyponitrite; should the test solution be strongly alkaline a holly-green colour, changing to red on acidification, is produced. In the same paper Corbet refers to the work of Wooldridge, who has found "that if the test solution is buffered at a *p*H value between 5 and 6 an *old gold colour* is developed immediately resorcinol and potassium iodate are added in presence of hyponitrite, whilst fainter pink colours are produced after an interval of one minute with borates and bicarbonates. The colour developed with hydroxylamine is of a deep reddish hue and not yellow."

As Corbet has not described any set of conditions under which a definite colour reaction is developed we have made detailed experiments to ascertain them. The results have shown that if the test is to be of any value, the *p*H must be controlled within very narrow limits. With dilute solutions of hydroxylamine hydrochloride or of a hyponitrite buffered at *p*H 2 a stable cherry-red colour develops within 3 to 5 minutes, the intensity of the colour and the time taken for the maximum intensity to develop depending on the concentration.

METHOD.—The following procedure is recommended:—Sørensen's buffer mixture (Clarke, *Determination of Hydrogen Ions*, 3rd Ed., 1928, p. 209) is prepared by treating 21·008 g. of citric acid with 200 ml. of *N* sodium hydroxide solution and making up to 1 litre. One ml. of the neutral solution under examination is treated with 4 ml. of this sodium citrate buffer followed by 2 ml. of the freshly-prepared reagent (made by mixing equal volumes of *M*/5 resorcinol solution and a saturated solution of potassium periodate). In the presence of hydroxylamine or hyponitrite a cherry-red colour develops in 3 to 15 minutes.

The results obtained in test experiments show that it is possible to detect 1 part per million of hydroxylamine hydrochloride or hyponitrite in an aqueous solution. At *p*H 3 borates and bicarbonates do not give this colour reaction. They may, however, interfere to some extent with the colour reaction for hydroxylamine and hyponitrite, owing to their capacity to alter the *p*H. Borates, when present to the extent of 2000 parts per million of water, do not interfere with the test. Bicarbonates may be destroyed by careful treatment with acid before the test is applied.

At *p*H values above 4 both hydroxylamine and hyponitrite in 0·01 per cent. solution gave only a yellow colour. At *p*H 4 a light orange-red colour was not obtained with a 0·01 per cent. solution of hydroxylamine hydrochloride until after 30 minutes. At *p*H 1 with a 0·001 per cent. solution a light orange-red colour was obtained after 5 minutes, changing to light yellow after 20 minutes, and to golden yellow after 35 minutes.

G. GOPALA RAO
W. V. B. SANDARA RAO

DEPARTMENT OF CHEMISTRY
ANDHRA UNIVERSITY
WALTAIR, INDIA

June 23rd, 1938

COPPER IN TOMATO PRODUCTS

FOR the determination of copper by the method of Cockburn and Herd,[1] using the sodium diethyldithiocarbamate reagent of Callan and Henderson,[2] it is essential that the solution, to which the reagent is to be added, should be free from any yellow or brown tint.

We have met with samples that do not yield a colourless solution on the final addition of ammonia, and have tried various methods of eliminating the interfering substance, which seems to be of the same character as that obtained, and subsequently guarded against, in the Ramberg[3] method for the determination of arsenic.

We have found that the difficulty it causes may be prevented by boiling the colourless acid digested mixture with 10 ml. of a saturated solution of ammonium oxalate previous to diluting with water and making alkaline with ammonia.

This suggests that during the acid digestion process, a nitro body is formed and that the treatment with the oxalate breaks this up and makes it possible to obtain a clear solution which can then be easily compared with standard copper solutions.

C. E. SAGE and S. G. E. STEVENS

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Notes from the Reports of Public Analysts

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

CITY AND COUNTY OF KINGSTON UPON HULL

CITY ANALYST'S REPORT FOR THE SECOND QUARTER, 1938

OF the 561 samples examined, 222 were taken informally.

ICE CREAM.—Six samples contained from 2·8 to 9·8 per cent. of fat, and three of them contained farinaceous matter. In one sample half of the 6·2 per cent. of the fat present was a fat other than butter-fat; it was returned as adulterated.

CHOCOLATE CAKES.—Four of 9 samples examined contained only trivial amounts of cocoa, and were returned as adulterated. Since these were the first cases of the kind in this area, the Chamber of Trade, the Wholesale Confectionery Section of the Chamber of Commerce, and other interests were notified that chocolate cakes would be required to contain a minimum of 4 per cent. of dry fat-free cocoa material.

UNGRADED MILK.—In spite of the Milk (Special Designations) Order, 1936, only slightly more than a third of the total quantity of milk sold in Hull is graded. It is to be hoped that before long even ungraded raw milk, intended for human consumption, will be required to conform at least to the bacterial standards of purity now laid down for accredited milk.

One of the most urgently needed reforms in Public Health Law is the further provision of regulations restricting the sale of milk to premises adapted for the purpose and to persons who have the experience and will to guard against its contamination.

ARNOLD R. TANKARD

CITY OF LEICESTER

REPORT OF THE CITY ANALYST FOR THE YEAR 1937

PORK DRIPPING.—A sample purchased under this name was found to contain 2·5 per cent. of free fatty acids. In subsequent correspondence with the manufacturer it transpired that the article was sent out as "Roast Pork Dripping with Jelly," each tin containing an upper layer of fat and a lower layer of jelly, constituting 7 to 10 per cent. of the whole. When it was cut through vertically, each purchaser would receive a representative proportion of the two constituents. The jelly portion contained several per cent. of free organic acid, and on storage some of this acid would diffuse into the fat layer. It was ultimately decided to adhere to the maximum standard of 1 per cent. of free fatty acid for edible fats, but to modify the standard to 2 per cent. of free fatty acids for an article with a qualifying description such as "Roast Pork Dripping with Jelly." This standard was acceptable to the manufacturer.

POTTED BEEF.—Two samples, containing over 74 per cent. of water, were reported against for excess of moisture. One had a firm consistence, due to the presence of gelatin, and the manufacturers stated that it should have been sold as "jellied potted beef." The other contained no gelatin and was soft and wet. As the average moisture-content of commercial samples is about 55 per cent., a maximum of 70 per cent. is considered a lenient figure to adopt.

"MILK AND CREAM CHEESE."—A formal sample was in the form of a sandwich. The two constituents were separated and analysed separately, with the following results:

	Milk portion Per Cent.	Cream portion Per Cent.	Average of total sample Per Cent.
Water	80·7	57·6	77·36
Total solids	19·3	42·4	22·64
Fat	0·56	23·3	3·84
Fat as per cent. of total solids	2·9	54·7	17·0

The milk portion constituted 85 per cent. of the whole sample. In view of its composition it was reported that the cheese as a whole was made from milk deprived of about 62 per cent. of its original fat, and should have been called "Skimmed Milk and Milk Cheese." Proceedings were taken and the vendor was fined £1. When the third portion was produced in Court it was several weeks old and was completely liquid.

F. C. BULLOCK

CITY OF LONDON

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1937

IN his report for 1937 the Medical Officer of Health for the City of London includes the details of the examination of the samples submitted to the Public Analyst (Mr. A. J. C. Lickorish). Of the 1007 samples examined, 759 were taken informally.

FORMALDEHYDE IN SMOKED BACON.—Early in the year a communication was received from the Medical Officer of Health of another local authority to the effect that samples of smoked bacon, taken and submitted to the Public Analyst of that district, had shown the existence of from 25 to 35 parts per million of formalin, and that some of the samples were from bacon which originated from a City bacon factory. "Preservative," which is defined by the Public Health (Preservatives, etc., in Food) Regulations, does not include "any substance added to food by the process of curing known as smoking." Inquiries were instituted at the premises of the City firm in question, where it was ascertained that the inner surfaces of the

sides of bacon are scraped, pea flour sifted over them, and the bacon immediately hung in the smoke-chamber and wood-smoked for about 48 hours or longer. It was felt desirable that an experiment should be made to ascertain the effect of smoking bacon. Accordingly, a gammon rasher was cut from a side of bacon before smoking, and the remainder of the side was then smoked in the usual manner. After removal from the chamber, two rashers were cut from the exposed end and the side was then divided, and another rasher was taken from one of the freshly-cut ends. These rashers were submitted for analysis, with the following results:

Sample	Formaldehyde p.p.m.
Rasher, cut before smoking	Nil
Rashers, cut from exposed end after smoking—	
(*a*) Outside and exposed rasher	16
(*b*) Next rasher adjoining	10
Rasher taken, after smoking, from freshly-cut surface of divided side	2

Four samples of smoked bacon purchased ordinarily in City shops showed similar small amounts of formaldehyde upon analysis.

METROPOLITAN BOROUGH OF STEPNEY

Annual Report of the Borough Analyst for the Year 1937

Of the 1544 samples examined, 584 were purchased informally.

Cream Cheese.—In 1936 the Public Health Committee authorised the Medical Officer of Health to inform purveyors in the Borough that it was an offence to sell soft cheese made from milk as cream cheese. Of 19 samples examined during 1937, fifteen were adulterated. Of these, two were hard cheeses, containing 20·0 and 20·8 per cent. of fat; twelve were soft cheeses, containing from 11·2 to 22·2 per cent. of fat; one sample, sold as "Double Cream Cheese," contained 14·4 per cent. of fat. Action was taken in three cases. The vendors of two soft cheeses made from milk were each fined £1 with £2 2s. costs, and the vendor of the "Double Cream Cheese" was discharged (with £5 5s. costs) under the Probation of Offenders Act.

Magnesia.—Three informal and two formal samples consisted of effervescent magnesium sulphate, and a formal and informal sample consisted of magnesium carbonate. The vendors of the formal samples were cautioned. D. Henville

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.

HYDROGEN CYANIDE IN RAISINS*

Between April 8th and 29th, 1937, the U.S. Attorney for the Northern District of New York, acting upon reports by the Secretary of Agriculture, filed in nine district courts libels praying seizure and condemnation of six different shipments of cases of raisins from California. It was alleged that the product contained hydrocyanic acid in amounts which might have rendered it injurious to health. On various dates from June 5th to July 8th, 1937, no claimants having appeared,

* U.S.A. Dept. of Agriculture. Notices of Judgment under the Food and Drugs Act, Nos. 27401, 27456, 27525. Issued January, 1938.

judgments of condemnation were entered and the product was ordered to be destroyed.

On May 18th, 1937, similar actions were brought by the U.S. Attorney for the Eastern District of Virginia in respect of 452 and 73 cases of raisins shipped from California. These were also condemned and destroyed.

On April 12th and April 14th, 1937, similar actions were brought by the U.S. Attorneys for the Northern and Eastern Districts of Virginia, in respect of 23 and 100 cases of "seedless" raisins, seized in the respective districts after shipment from California. On July 13th and October 14th, 1937, no claimant having appeared, the products were condemned and destroyed.

Department of Scientific and Industrial Research

REPORT OF THE FOREST PRODUCTS RESEARCH BOARD FOR THE YEAR 1937*

THIS Report gives a general survey of the progress of research in connection with the use of timber. During the year reviewed more than 200 new species have been added to the Laboratory's collection of timbers, bringing the total number to 4065. The recent acquisitions have come principally from the Federated Malay States, Tanganyika Territory, British East Africa, and the Cameroons. An account is given by the Director of Research (Mr. W. A. Robertson) of the special scientific investigations that have been undertaken; these include the following:

MOISTURE-RESISTANCE OF PAINTS.—A method of testing moisture-resisting qualities of paints on wood has been developed; it consists in exposing pairs of matched panels of beech to standard humidity changes. One of the panels is painted and the other is left uncoated; and the efficiency of the coating is assessed by comparing the moisture-content changes in the treated and untreated panels. With gloss oil paint, the efficiencies for seven, fourteen and twenty-eight day periods were found to be 85, 75 and 60 per cent. with one coat, and 95, 92 and 86 per cent. with two applications. Analogous results were obtained with heavy bituminous paints. The low moisture-resisting value of boiled oil has frequently been pointed out, but the fact does not seem to be sufficiently well known to the trade. The beneficial effect of the second coat was indicated by tests with aluminium paste in a spar varnish medium. The seven-day efficiency of one coat was 25 per cent., whereas the corresponding figure for two coats was over 75 per cent.

FIRE-RESISTANCE OF TIMBER.—The action of the compounds that cause wood merely to char has generally been assumed to be as follows:—

(1) The compound melts at a temperature below that at which the timber would normally burn, and forms a glaze preventing access of oxygen to the wood.

(2) The compound decomposes under the influence of heat yielding inert vapours or gases which dilute the combustible gaseous products of the wood to such an extent as to render the mixture non-inflammable.

(3) Under the influence of heat the compound vaporises or dissociates, with sufficiently large absorption of heat to prevent the temperature of the wood rising high enough for it to decompose.

There is no doubt that all these phenomena may contribute to the effect of a fire-proofing compound, but from general observation during the testing of such compounds it was considered that they did not completely account for the whole of the fire-proofing effect.

* H.M. Stationery Office, York House, Kingsway, London, W.C.2 Pp. 83. 1938. Price 2s. net.

It was noted during these tests that a harder, denser charcoal was formed from treated material than that from the untreated material. It is known that in carbonising wood the yield of charcoal can be increased by the addition of certain chemicals and it was thought that this same action might be responsible for a fire-resisting effect. A series of experiments based on this supposition was carried out to determine the effect of a number of chemicals on the yield of charcoal during carbonisation. It was found that several chemicals increased the charcoal yield by as much as 100 per cent. and that all the chemicals that had this property were known to be capable of increasing the fire-resistance of timber, whereas those that did not increase the yield of charcoal were of the type known to have very little fire-retarding effect. The increase in charcoal yield must be at the expense of the inflammable volatile products of distillation, and it is reasonable to assume that this effect is the major action of a fire-proofing compound. The other factors, such as the evolution of inert gas, formation of glaze, and absorption of heat no doubt also play a part, but only to a minor extent.

Examination of the salts which have the effect of increasing the charcoal yield showed that they were all of the type which decompose under the influence of heat, with the formation of the acid from which the salt is derived. The stable salts had very little effect. At first borax, which is an effective salt and is also stable under ordinary conditions, was thought to be an exception, but there is definite evidence that borax heated in the presence of methyl alcohol (one of the products of wood carbonisation) dissociates, yielding the free acid.

SEASONING OF TIMBER.—The Laboratory has developed an improved type of seasoning kiln which should be of great benefit to the industry. The question of the materials which could be suitably employed had an important bearing on the design. It was found, for example, that bituminous paint is excellent for the brickwork and for much of the metal work, but that it flakes rapidly when applied to the heating pipes. For painting these the greatest success has been obtained by using an undercoat of aluminium paint, and following this with a paraffin-soluble anti-rust composition.

As regards the fundamental research on seasoning, it has been known for some time that timbers such as oak and beech can be darkened by steaming at 212° F. As it is not always practicable to employ so high a temperature, experiments have been conducted to discover the effect of steaming at lower temperatures. The results with beech have proved very satisfactory, steaming at 176° F. producing the same effect in forty-eight hours as it does in twenty-four hours at 212° F. The report adds that: "For oak, the additional time required is so great as to make the process uneconomical, and this wood should therefore be steamed at 212° F. to give the desired result."

PROTECTION OF TIMBER AGAINST BEETLES.—In the report for 1936 it was recorded that oak sapwood immersed for five minutes in a 20 per cent. solution of a chlorinated naphthalene wax in benzene and exposed two months later to *Lyctus* beetles was not attacked by these insects. Further tests have shown that such a treatment will prevent infestation by *Lyctus* for at least nine months. Samples treated with a mixture of one part of creosote and two parts of paraffin have resisted *Lyctus* for 11 months after treatment, but this preservative has the disadvantage of discolouring the timber. A further series of experiments, using a wider range of absorptions, has been started with a 5 per cent. aqueous solution of potassium chromate as preservative.

It is pointed out that there is no evidence to support the common belief that the use of incense in a church protects the roof beams from the attack of the death-watch beetle.

THE HEMICELLULOSES OF OAK WOOD.—Research work on the fractionation of the hemicelluloses of oak wood has been continued. The fraction of hemicellulose A (from both sapwood and heartwood) which is insoluble in water at

100° C. has been further fractionated by digestion with the enzyme takadiastase, under carefully controlled conditions, into an insoluble polysaccharide, a soluble polysaccharide and the reducing sugar glucose. The most important result of this further fractionation has been that the polysaccharide which is not brought into solution during digestion with the enzyme has a specific rotation of −97·5° in every instance. This result, in conjunction with certain analytical evidence, suggests that there is a polysaccharide fraction which is common to the hemicellulose A of both the sapwood and heartwood of oak.

In addition to wood starch, at least two water-soluble polysaccharides which are related to starch are known to occur in oak sapwood. It has been found that all these related bodies, as well as a number of oak hemicellulose preparations, contain uronic anhydride groups. The chief fundamental significance of the uronic anhydride group is that it may represent a stage in the synthesis, within the tree, of certain major components, notably the hemicelluloses and lignin.

Action of Certain Oxidising Agents on Wood.—It is well known that, at high concentrations, hydrogen peroxide causes a rapid decomposition of wood. In the presence of alkali and at comparatively low concentrations, however, this reagent has a bleaching action which is finding an increasing application commercially. The early work of Marggraf (*Kunststoffe*, **1917**, **7**, 165) has been extended and detailed analyses have been made on both light- and dark-coloured woods before and after bleaching under various conditions. The results indicate that hydrogen peroxide (20 vols.) in the presence of ammonia can effect bleaching in a large number of woods, irrespective of their initial moisture-content or colour. Bleaching for periods up to 24 hours at room temperature results in the removal of minor components and the decomposition of part of the lignin. Prolonged bleaching ultimately leads to the decomposition of the wood cellulose. From the practical standpoint it is clear that a considerable degree of surface bleaching of wood in the piece by means of hydrogen peroxide and ammonia can be achieved without risk of serious chemical disintegration. Further, the final colour of the bleached material is reasonably permanent, provided drying is carried out at temperatures not exceeding 40° C.

When certain woods are warmed in the presence of a concentrated solution of potassium permanganate, a spontaneous and vigorous decomposition of the wood substance ensues. Analyses indicate that this reagent has the same order of chemical effect on wood as alkaline hydrogen peroxide, but no bleaching effect is produced.

Use of Synthetic Resins for Laminated Wood Products.—The use of synthetic resins as adhesives and impregnating media for laminated wood products has conferred on these moisture and heat-resisting properties and a stability hitherto unattained. The scope of the utility of laminated wood has thus been considerably increased, especially in connection with the manufacture of aircraft. Similar developments in the manufacture and use of compressed laminated wood, in which varying degrees of compression and impregnation with synthetic resin solutions are used to render the finished material suitable for special purposes, have added further interest to this class of product.

Adhesives of the glyptol-resin and latex-casein type allow of sufficient flexibility of the glue layer to overcome the difficulty arising from marked variations in the coefficient of expansion in other types of binding material. As the result of contact with the Research Association of British Rubber Manufacturers veneer has been supplied to them for tests of the suitability of rubber shellac composition as a bonding material for laminated wood. The moisture-resisting and insulating properties as an adhesive are of special interest.

Parallel with the use of synthetic resins as impregnating media, their employment as finishing materials in lacquer and paint form for wood has made equally rapid strides.

New South Wales

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1936

In his Annual Report the Government Analyst (Mr. S. G. Walton) states that 33,758 samples were examined in the Chemical Laboratory, representing an increase of 2676 on the number examined in 1935. This total included 31,583 samples submitted under the Pure Food Act and 2175 examined for other Government Departments.

During the recent Milk Inquiry information was sought by the Milk Commissioner as to the loss of milk occurring during the process of cooling as practised at the receiving depots in the country.

Loss of Weight of Milk on Cooling and Pasteurising.—The experiments were made on the premises of the Dairy Farmers' Co-operative Milk Co., Ltd., by the Assistant Government Analyst in conjunction with the Chief Food Inspector, an officer of the Weights and Measures Department and officers of the Dairy Farmers' Co-operative Milk Co., Ltd. The temperature of the milk at each weighing was taken at 55° F. by means of a thermometer having a N.P.L. certificate of accuracy to 0·1° F. The loss in weight of 5146½ lb. of milk, after cooling from 55° to 34° F., pasteurising and holding for 30 minutes at 145° F. and cooling to 40° F. was found to be 64½ lb. or 1·25 per cent. by weight.

The analyses of two 1-lb. samples of milk withdrawn were as follows:

	Total solids Per Cent.	Fat Per Cent.	Solids-not-fat Per Cent.	Freezing-point °C.
Raw milk	12·21	3·5	8·71	—0·54
Pasteurised milk ..	12·31	3·55	8·76	—0·545

Weight of One Gallon of Milk at Varying Temperatures.—At the request of the Milk Commissioner work was carried out to establish the weight af an Imperial gallon of milk at various temperatures. In each test 5 gallons of pasteurised milk were placed in a certified 5-gallon measure and weighed on a balance, supplied by the Weights and Measures Department, having an accuracy of 2 grains. The pasteurised milk had the following composition:—Total solids, 12·31; milk-fat, 3·55; solids-not-fat, 8·76 per cent. Freezing-point —0·545° C. The atmospheric temperature during the experiments ranged from 68·0° to 69·2° F., and the humidity from 55·0 to 61·0 per cent. The weight of 1 gallon of the milk at 42·5° F. was 10 lb. 5 oz. 7 drs. 2 grs.; at 55° F. it was 10 lb. 5 oz. 2 drs. 23 grs.; at 77·5° F. it was 10 lb. 4 oz. 9 drs. 7 grs.

Crude Fibre in Wholemeal Bread.—A number of samples of alleged wholemeal bread were found to have a crude fibre content (calculated on the dry substance) of less than 1·6 per cent. Several prosecutions were successfully undertaken by the Department. As a result of further work it was recommended that the standards for crude fibre should be amended. It is considered that whole wheat flour should contain not less than 2 per cent. of crude fibre (as determined by the A.O.A.C. method of analysis), whole wheat bread not less than 1·6 per cent., and brown bread not less than 1·2 per cent. (calculated on the moisture-free substance). It was also recommended that salt, milk, malt and carbohydrate sweetening substances may be added to any variety of bread; also that flour intended solely for bakers' use may contain specified amounts of acid calcium phosphate, ammonium chlorides, bromates and calcium sulphate. The presence of persulphate in any form is prohibited.

Enamel Ware.—As the result of an investigation of the enamel ware being offered for sale in New South Wales, it was recommended that a standard similar to that adopted by the London County Council (*cf.* Analyst, 1935, **60**, 217) should be incorporated as a regulation under the provisions of the Pure Food Act. Of

21 samples of enamel ware examined, 10 conformed to the proposed solubility limits; of these 10 five were free from injurious substances, and five contained antimony.

STANDARDS FOR ICES.—Many of the samples examined were sold under names intimating that they were the products of various fruits, milk, etc., but in a large proportion of these the amount of fruit, etc., was negligible. It was therefore decided to introduce a standard requiring fruit ice blocks to contain not less than 3 per cent. of fruit juice, and milk ice blocks to contain not less than 50 per cent. of milk. It was observed that when artificial colour is used in the preparation of ice blocks the colour is much less noticeable after freezing. Hence preparations now on the market contain a comparatively large amount of artificial colour. It is suggested that consideration might be given either to the elimination of artificial colouring matter or to limiting the permissible amount.

ARTIFICIAL COLOUR IN "SMOKED" MEAT.—The trade is continuing the practice of preparing "smoked" meat (legs of mutton) by the use of artificial colouring matter (Bismarck brown, etc.) During the year several prosecutions were recommended with a view to stopping this practice.

MENTHOL LINIMENT.—Owing to the trade restrictions imposed by the Commonwealth Government on imports from certain countries, manufacturing chemists found it impossible to obtain supplies of natural menthol for pharmaceutical preparations, and as a substitute were obliged to use synthetic menthol. This substance was not recognised by the British Pharmacopoeia, and its use, therefore, constituted an infringement of the provisions of Regulation 68 of the Pure Food Act. A sample of liniment of menthol was submitted for examination, and was found to have been prepared with the synthetic substance. As a result of representations made by this Department to the manufacturing firm concerned, arrangements were made with the Customs authorities to permit of the importation of natural menthol.

NITROBENZENE POISONING.—In a brief resumé of the work of the laboratory, dated 21st December, 1936, attention was drawn to a death occasioned by swallowing a dye preparation containing a considerable quantity of nitrobenzene. The fact was brought to notice that this preparation was in common use, and it might, therefore, be considered advisable to add nitrobenzene and preparations containing more than a specified percentage of this substance to the Second Schedule of the Poisons Act. This procedure has since been followed, with the result that nitrobenzene and preparations containing more than a definite percentage of this substance can now be sold only by a person with a licence to sell poisons, and the container must be labelled "Poison." Since the death referred to above, two further deaths have been recorded from this substance, the result, doubtless, of the publicity given to the first death.

DOPING OF RACING DOGS.—Exhibits submitted in connection with the doping of racing dogs were found to contain cocaine hydrochloride, caffeine, phosphorus, extract of nux vomica, extract of damiana, ether, tincture of digitalis and glycerophosphates.

The assistance of the laboratory was also sought in connection with a case of alleged "ringing in" of greyhounds. Examination of the exhibits of hairs submitted showed that some of the animals had been dyed, and convictions were obtained.

DETERMINATION OF ALCOHOL IN BLOOD AND URINE.—Since the publication of the method in the Annual Report for 1935 (ANALYST, 1937, **62**, 612) there has been an increase in the number of exhibits submitted for examination. The specimens generally were taken either from the drivers of motor vehicles involved in accidents, or from persons knocked down by motor vehicles, in many instances fatal results having ensued. It is desirable that in all motor accidents having fatal results, an examination of the urine and blood of the deceased person or

persons and, if possible, of the driver of the vehicle, should be made. This procedure should also be followed in cases of accident where the injury does not result in death. If the chemical examination proves that the injured person had been drinking, it is evidence in favour of the motor driver, whilst, on the other hand, if the analysis proves that the driver had been drinking it definitely strengthens the case against him. It is understood that it is the intention of the Government Medical Officer to have specimens of blood and urine examined in future in all fatalities due to motor accidents, in order to assist the coroner in his findings.

QUININE POISONING.—In a fatal case of quinine poisoning in which a woman took a large amount of the drug, several days elapsed before death occurred; nevertheless 0·01 grain of quinine was found in the stomach and contents, and 0·08 grain in the organs submitted.

Siam

EIGHTH REPORT OF THE DEPARTMENT OF SCIENCE

THIS report covers the period from April 1st, 1934, to March 31st, 1936. During the two years there was a notable increase in all branches of work and a number of qualified Siamese were added to the staff as Assistant Chemists. The only European member of the professional staff is the Senior Chemist, Mr. C. J. House, F.I.C.

The total number of samples examined was 35,628, as compared with 13,872 during the previous period, the increase being largely due to increased activity in the control of opium dross. Of the 347 samples examined for the Department of Public Health, 265 were samples of water. The only samples of food examined for that Department were 11 of milk. Two hundred samples of tinned or dried milk were also submitted by the Customs Department.

NOTES ON POISONING CASES.—In the 54 cases investigated, poison was detected in 30. Datura was found in 8 cases, arsenic in 6, strychnine in 4, sodium cyanide in 3 and hydrochloric acid in 2.

Poisoning by Meliantha suavis (*Pak wan*).—A case of poisoning was reported from Kanburi district, where eight people lost their lives by eating the leaf-shoots as food. The chemical nature of the poison awaits investigation.

Poisoning by Japanese Star Anise (*Illicium religiosum*).—In March, 1935, the Bangkok police reported that a Chinese had died after eating star anise fruits. It was found that two varieties of star anise were offered for sale in certain Chinese drug shops, *viz.* the normal variety, *Illicium verum*, and the Japanese star anise, *Illicium religiosum*. A certified specimen of the latter was obtained from the Botanical Garden, Tokyo University, and its characteristics were compared with those of the normal plant. The fruits of *Illicium religiosum* have a balsam-like odour and a salty taste, the peduncle is straight, and the carpel is poorly developed and points upwards. An alcoholic extract gave negative results for alkaloids and glycosides.

ACT TO CONTROL THE QUALITY OF PEPPER.—Early in 1935 a Committee was formed to find a means of protecting the quality of Siamese pepper in the world's export markets, and on their recommendation a law was passed in April, 1936, making it an offence to attempt to export adulterated pepper or pepper having an excessive moisture-content. Later a Ministerial Decree fixed the statutory limit for moisture at 15 per cent. and prescribed directions for its determination. In the Customs laboratory the Schopper moisture tester is to be used at 110° C., but if the statutory limit is exceeded or approached, the testing office is directed to send a sample to the Department of Science for more accurate determination. With such samples a correction for volatile matter, other than moisture, lost at 110° C. would be applied.

KRATOM (*Nitragyne Speciosa*).—The investigation of this plant has continued to arouse interest in Siam, as the opinion is sometimes expressed that the habit of chewing the leaves is harmful and should be repressed by legislation. The physiological action was fully discussed in the 6th Report (*cf.* ANALYST, 1934, **59**, 753), and on this aspect there is nothing further to report. Dr. H. R. Ing, of University College, London, who is working on the problem of isolating alkaloids other than nitragynine, has found that the method of purifying the nitragynine alkaloid by crystallisation of the picrate from hot acetic acid leads to a continuous degradation of this alkaloid to amorphous products, resulting in small yields; no other alkaloid has yet been isolated in a crystalline form. As there is some doubt whether the ethyl alcohol used to extract the leaves may not have some action on these alkaloids, the investigation is to be continued with the dried leaves instead of an alcoholic extract as the original material.

MAI CHANCHAMOT (PERFUMED WOOD).—The wood derived from decayed trees of the species *Mansonia gagei* has a musk-like odour, and is known in commerce as *Mai Chanchamot* (civet sandal wood). As described in the 7th Report (*cf.* ANALYST, 1936, **61**, 846) a crystalline odorous principle was isolated in the Imperial College of Science and Technology by Dr. R. P. Linstead, and a preliminary report has been received upon it from Professor J. F. Thorpe. The substance (m.p. 139° C.) is colourless and has a strong odour of sandal wood. Its most probable formula is $C_{15}H_{18}O_3$, and one of the oxygen atoms is in a methoxy (or methyl ester) group. Further work on the oxidation products is in progress.

SEA-WEED OF *Gelidium* SPECIES.—A sample from Songkla was investigated to ascertain if a more merchantable product could be prepared. The present material is used to prepare jellies. It is prepared by washing and bleaching in the sun along the sea coasts of the Gulf of Siam, but the local product is often dark in colour and unpleasant in odour. Treatment with animal charcoal followed by filtration yielded a product which closely resembled jelly made from commercial agar agar. This could be dried to thin blocks for storage, although the drying process caused deterioration in colour. Japanese agar is concentrated by freezing the jelly during the winter season—a method which cannot be applied in Siam.

Arsenic in Brewing Materials

REPORT OF THE SUB-COMMITTEE OF THE STANDING COMMITTEE OF THE INSTITUTE OF BREWING

THE Sub-Committee formed by the Standing Committee for Analysis to investigate the methods for the estimation of arsenic in brewing materials consisted of A. E. Case, H. Heron and A. J. C. Cosbie. It has now issued its report.*

After consideration of the methods proposed or in use it was concluded that those involving conversion of the arsenic into arsine were the most applicable to brewing materials, and the investigation was confined to these. The Marsh–Berzelius and Gutzeit tests were studied, and a technique was adopted which enabled a close comparison of the two methods to be made under varying conditions. For the Gutzeit test the disc system, in which the amount of arsenic is measured by the colour and intensity of the stain, appeared to be more satisfactory than the strip system (*cf. J. Soc. Chem. Ind.*, 1907, **26**, 1115) for determining small quantities (less than 0·01 mg.) of arsenic.

Mercuric bromide (*cf.* Kemmerer and Schrenk, *Ind. Eng. Chem.*, 1926, **18**, 707) was found to give a deeper colour and to be more sensitive than mercuric chloride. The useful range for the two sensitising agents was found to be 0·001 to 0·01 mg.

* *J. Inst. Brewing*, August, 1938, **44**, 359–361.

of As_2O_3 for the chloride, and 0·0004 to 0·004 mg. for the bromide. On the other hand, as the bromide is less stable, its use demands more precise methods of impregnating the paper than the use of the chloride.

The following conclusions were drawn from comparative determinations by the Marsh–Berzelius and Gutzeit methods:

(1) The lower useful limits of sensitivity were: Marsh–Berzelius, 0·001 mg.; Gutzeit, 0·0004 mg.; useful upper limits, Marsh–Berzelius, 0·02 mg.; Gutzeit, 0·004 mg. (as As_2O_3).

(2) The Marsh–Berzelius stain was permanent up to 3 months if sealed in dry hydrogen. The Gutzeit stain was unsatisfactory for any considerable period, but could be matched by factitious water-colour standards (*cf.* Henley, *J. Inst. Brewing*, 1928, 608).

(3) The Marsh–Berzelius stains show variation in intensity and length, whilst the Gutzeit stains show variations in intensity and colour; for this reason the latter are usually more easily evaluated than the former.

The Gutzeit test has been adversely criticised, *e.g.* by Chapman, Monier-Williams, Aumonier, and others, and the Government Laboratory uses the Marsh–Berzelius test. On the other hand, the Gutzeit test is the method of the British Pharmacopoeia and is advocated by the Sub-Committee on the Determination of Arsenic, Lead and other Poisonous metals in Food Colouring Material, convened by the Analytical Methods Committee of the Society of Public Analysts (ANALYST, 1930, **55**, 102).

The objections to the Marsh–Berzelius test are: (1) the difficulty of securing regular supplies of suitable glass; (2) the necessity for the complete exclusion of air (oxygen); (3) intensity and length of stain to be measured. Having regard to these difficulties, especially (1), it was decided to concentrate on the Gutzeit test and to study all the factors, whilst at the same time comparative tests were made by the electrolytic Marsh–Berzelius method.

As the result of these investigations an accurate technique was established and comparison with the electrolytic method showed that satisfactory blank tests could be obtained regularly by either method.

After further research a technique applicable to hops, malt, beers, sugars and finings, and also to malting coals, was devised. The method (*vide infra*) recommended does not require previous destruction of organic matter, and if the details are closely followed can be made to give results of a high degree of accuracy for the brewing materials specified.

THE DETERMINATION OF ARSENIC IN BREWING MATERIALS*

PREPARATION OF MATERIAL:—*Coal.*—A representative sample is finely powdered in an agate mortar, and 0·5 g. is mixed, by grinding, with 0·5 g. of a mixture of equal weights of potassium permanganate and magnesia, and introduced in an even layer into a Vitreosil boat (100 × 10 mm.) containing a bottom layer of magnesia (0·15 to 0·2 g.). The boat is placed in a Vitreosil combustion tube (20 mm. in diameter and with one end reduced in width), and a current of oxygen is passed through the tube, which is heated with a Bunsen burner fitted with a flame spreader. After ignition is complete (about 5 minutes) the boat is transferred to a 100-ml. beaker and, after cooling, the ignited mass is washed out of the boat with a little water. One ml. of conc. sulphuric acid and 2 ml. of a 30 per cent. solution of oxalic acid in industrial spirit are added, and the liquid is gently boiled for 5 to 10 minutes, after which it is allowed to cool, diluted to 50 ml., and transferred to the Gutzeit reaction bottle.

* A. E. Case, *J. Inst. Brewing*, 1938, **44**, 362–374.

Sugar.—Twenty-five ml. of a 10 per cent. solution are measured into the Gutzeit bottle, and 25 ml. of water and 1 ml. of 25 per cent. sulphuric acid are added.

Malt.—Ten g. are treated with 100 ml. of boiling 0·5 per cent. sulphuric acid, and the mixture is left to cool (about 1 hour) with frequent stirring. Fifty ml. of the supernatant liquid (poured through a filter-plate) are introduced into the Gutzeit bottle.

Hops.—Five g. (taken from the middle of the sample) are treated with 250 ml. of boiling 0·5 per cent. sulphuric acid as described for malt, and 50 ml. of the supernatant liquid are taken for the test.

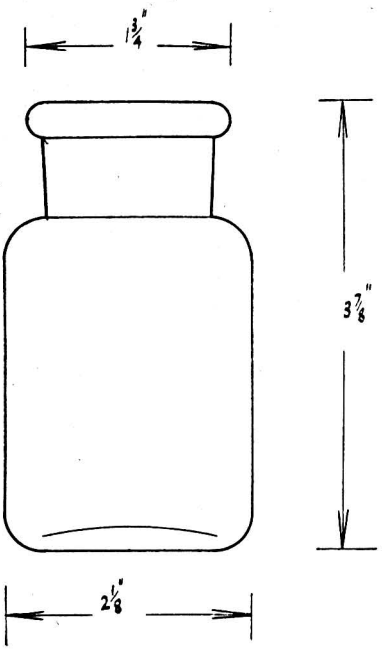

Fig. 1

Beer.—If the original gravity was lower than 60°, fifty ml. are measured into the Gutzeit bottle and 1 ml. of 25 per cent. sulphuric acid is added. If the original gravity was higher than 60°, twenty-five ml. are taken, and 25 ml. of water and 1 ml. of 25 per cent. sulphuric acid are added.

Finings.—One hundred ml. are diluted to 500 ml. with water; 50 ml. are measured into the Gutzeit bottle and 1 ml. of 25 per cent. sulphuric acid are added.

THE GUTZEIT APPARATUS.—This consists of a 4-oz. wide-necked bottle of the dimensions shown in Fig. 1, the details of which are shown in Figs. 2 and 3. The bung should be extracted for 3 days in a boiling water-bath with 5 per cent. sulphuric acid, the acid being renewed each day. The bung is then well washed with water and bored to receive the delivery tube, which is 6 in. long, 8 mm. in external, and 6 mm. in internal diameter. A special fitting is provided to hold the Gutzeit fitting.

The Gutzeit fitting (Fig. 2) consists of a bakelite cylinder $\frac{7}{8}$ in. long, of $\frac{9}{16}$ in. radius, and bored centrally with a hole exactly $\frac{1}{4}$ in. in diameter from the top and a hole $\frac{5}{8}$ in. in diameter from the bottom, each to a distance of $\frac{7}{16}$ in. The top of the fitting is flat and polished, and for a depth of $\frac{1}{4}$ in. from the top the cylinder is threaded to take the screw cap. The lower internal surface of the cap is flat and the outer edge is milled. The cap is bored centrally with a hole $\frac{1}{4}$ in. in diameter and is threaded internally to fit on to the cylinder. The cylinder is fitted on the glass delivery tube by means of rubber pressure tubing ($\frac{7}{16}$ in.).

THE GUTZEIT REACTION.—To the 50 ml. of liquid in the bottle are added:—(*a*) 5 ml. of 5 per cent. potassium permanganate solution and 5 ml. of water for coals. (*b*) Ten ml. of 5 per cent. potassium permanganate solution for sugars, malts, hops, beers or finings. The mixture is well shaken, left for 30 minutes, again shaken and again left for 30 minutes. Two ml. of 50 per cent. sulphuric acid followed by 5 ml. of a 50 per cent. solution of invert sugar in 4 per cent. hydrochloric acid are then added (to remove the excess of permanganate and manganic oxides; excess of sugar does not interfere). After standing for 30 minutes the bottle is again well shaken and again left for 30 minutes. One ml. of a solution of 50 g. of potassium iodide solution and 4 g. of sodium sulphite ($Na_2SO_3.7H_2O$) per 100 ml. are then added, the reaction mixture is shaken with a rotatory motion, and the bottle is allowed to stand for at least 1 hour. Fifteen ml. of "caseinated" acid are added. (This is prepared by adding 25 g. of B.D.H. "light white soluble" casein to a mixture of

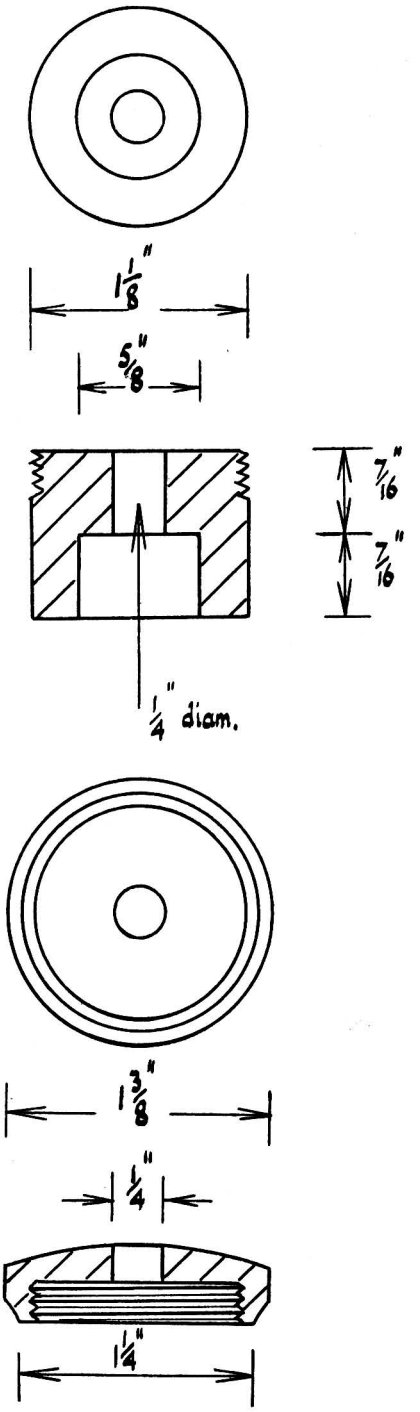

Fig. 2

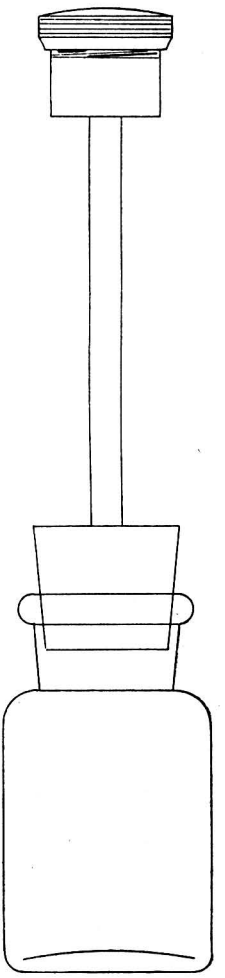

Fig. 3

500 ml. of sulphuric acid and 500 ml. of water at 85° C., shaking the flask for 10 minutes and cooling it rapidly in running water; it is ready for use after 24 hours; its use controls the rate at which nascent hydrogen is produced.) After 1 hour 1 ml. of a 2 per cent. solution of sodium sulphite and 1 ml. of recently prepared 5 per cent. stannous chloride solution (50 g. of stannous chloride are dissolved in 100 ml. of 10 per cent. hydrochloric acid, and 10 ml. of this solution is diluted to 100 ml.) is added, followed by 15 g. of zinc (about 5 to 6 pieces; the size is important). The mixture is quickly shaken round, 2 ml. of purified amyl alcohol (*infra*) are added, and the prepared Gutzeit tube is attached by pressing the bung tightly into the bottle. The apparatus is allowed to stand overnight covered with a sheet of paper to prevent access of light, the papers are then removed, and the stains are compared with the prepared standards, and the arsenic figures may be read from a prepared chart.

The amyl alcohol is purified by treating 250 ml. of the alcohol with 25 ml. of 50 per cent. sulphuric acid in a separating funnel, and extracting the solution three times with 100-ml. portions of water.

Standard Solutions of Arsenic.—Potassium hydrogen arsenate (0·433 g.) is dissolved in water and the solution is diluted to 1 litre (= 0·0238 per cent. of As_2O_3 or 100/6 grains per gallon). Ten ml. of this solution are diluted to 1 litre, giving solution "A" containing $\frac{1}{6}$ grain of As_2O_3 per gallon (1 ml. = 0·00238 mg. As_2O_3). For convenience a series of standard solutions (1 to 11) is prepared so that 2 ml. of each solution may be used in the preparation of the standard stains.

Standard No.	As_2O_3 grains per gallon	Amount of solution "A" equiv. to 2 ml. of standard ml.
1	1/60	0·2
2	1/48	0·25
3	1/40	0·3
4	1/34·3	0·35
5	1/30	0·4
6	1/24	0·5
7	1/20	0·6
8	1/16	0·75
9	1/12	1·0
10	1/10	1·2
11	1/8	1·5

In preparing the standard stains 2 ml. of the As_2O_3 solution are run into 50 ml. of 5 per cent. pure sucrose solution in the reaction bottle, 1 ml. of 25 per cent. sulphuric acid is added, and the procedure described above is followed.

Treated Cotton Wool.—Ten g. of absorbent cotton wool of good quality are spread out in a whole-plate developing dish, and 40 ml. of a well-shaken 5 per cent. suspension of basic lead acetate in a 15 per cent. (by vol.) solution of glycerin in industrial spirit are poured over it as evenly as possible, the wool being squeezed to assist distribution of the suspension, during which process the total weight is reduced to about 40 g. The wool is then spread out and allowed to dry, fresh surfaces being exposed at intervals. When practically all the spirit has evaporated (a day may be necessary) the wool is transferred to a desiccator (containing 80 per cent. by vol. sulphuric acid) for storage. It is kept there at least overnight before use.

Gutzeit Papers.—Discs, 1 in. in diameter, are cut by means of a cork borer from Whatman No. 130 filter-paper, and put on a piece of plate glass in a shallow glass or earthenware dish. Four to 5 drops (0·075 ml.) of a solution of 4 g. of mercuric bromide in 100 ml. of acetone (AnalaR) are made to fall across each paper.

Then without disturbing the papers, the upper surfaces of which have been marked with a pencil, the dish is transferred to a desiccator (80 per cent. sulphuric acid) and allowed to remain in the dark for not less than 2 or more than 24 hours before use.

Dry Protective Backing Papers.—These papers, used to protect the impregnated papers from light and atmospheric humidity during the actual test, consist of 1 in. circles cut from Ford blotting paper (428 Mill, 80 lb. wt. per ream demy) or a blotting paper of similar thickness.

STANDARD STAINS.—A series of 11 synthetic stains is prepared consisting of chrome yellow, orange chrome and burnt umber pigments in varying amounts on the actual filter circles used in the test, and corresponding to the quantities of arsenic in the following table. For this purpose a large number of synthetic stains must be prepared and the best matches with the actual standard stains selected. Standards thus prepared will not fade and may be conveniently mounted on a card with the following table:

Stain No.	As_2O_3 mg.	Standard arsenic sol. "A" ml.	Beers 50 ml. Malts 5 g.	Beers 25 ml. Sugars 2·5 g.	Finings 10 ml. Hops 1 g.	Coals 0·5 g.
1	0·00048	0·2	1/1500	1/750	1/300	1/150
2	0·00060	0·25	—	—	—	—
3	0·00071	0·3	1/1000	1/500	1/200	1/100
4	0·00083	0·35	—	—	—	—
5	0·00095	0·4	1/750	1/375	1/150	1/75
6	0·00119	0·5	1/600	1/300	1/120	1/60
7	0·00143	0·6	1/500	1/250	1/100	1/50
8	0·00179	0·75	1/400	1/200	1/80	1/40
9	0·00238	1·0	1/300	1/150	1/60	1/30
10	0·00286	1·2	1/250	1/125	1/50	1/25
11	0·00357	1·5	1/200	1/100	1/40	1/20

Grains per lb. for malts, sugars, hops and coals. Grains per gallon for beers and finings.

A determination with Standard No. 3 is made on every batch, as it is susceptible of more accurate reading than the blanks. If the stain in the test is less than stain No. 1 the result is recorded as less than the respective amounts in the first line of the table. If the stain is greater than No. 11 the test is repeated on half (or other) concentration of the material.

PREPARATION OF THE GUTZEIT TUBES.—Two separate plugs of the treated wool (*supra*) are packed by means of forceps and two pieces of cane into the delivery tube. The upper plug ($\frac{1}{2}$ in. long) is moderately tight and is compressed from the upper and lower ends. It is so placed in the tube that it prevents access of light to the impregnated paper from the underside. A second plug (1 in. long), which of course cannot be compressed, is placed in the lower part of the tube (3 in. from the bottom). Tubes should be repacked before each test, the old plugging being forced out from the cap downwards, thus automatically cleaning the tube. The impregnated paper is then placed in position, marked side uppermost, upon the polished surface of the fitting, covered with a backing paper and a brass washer (1 in. in diameter, $\frac{1}{4}$ in. hole), and the cap is screwed down until a joint is made. The completed units are kept in a desiccator (80 per cent. sulphuric acid) until required.

ACCURACY OF THE METHOD.—Stains can be evaluated with an accuracy equivalent to half the difference between adjacent standards. The maximum errors in terms of the standard solution "A" are therefore: 0·05 ml. for stains 1 to 7; 0·10 ml. for stains 7 to 10; 0·15 ml. for stains 10 to 11.

EFFECT OF TEMPERATURE.—The rate of stain production depends upon the temperature. Identical curves were obtained with beers and the standards at 80°, 70°, 60°, and 50° F. The time necessary to make a test can therefore be shortened, if desired, without great loss of accuracy, if a factor determined from a table or graphs (given in the original communication) is applied. For ordinary routine work, however, the overnight period of standing (16 hours) has been found most convenient, since it eliminates the necessity for strict control of temperature and time.

British Standards Institution

THE following Standard Specification has been issued:*

No. 804—1938. CRUCIBLE SWELLING TEST FOR COAL.

Several tests which are employed in the routine analysis of coal give some indication of its swelling power, but as these tests have been devised primarily for other purposes the measure of swelling power provided is not sufficiently discriminating. For this reason a crucible test, which has been devised solely to give some comparative measure of the swelling properties of coals, has been standardised.

The Crucible Swelling Test is based on the method devised in the laboratories of the Woodall-Duckham Companies (*Gas J.*, Nov. 9, 1925, Coke Competition Number, **30**, p. 15), and has been standardised by a series of tests in a number of laboratories using a wide variety of coals. Its special value as compared with other crucible tests lies in the use of a crucible of special shape, of a levelled coal surface, and of standardised unidirectional heating by means of a gas flame, with the result that a button of regular shape is obtained which can be simply assessed by comparison with standard outlines.

From a consideration of the average error it has been ascertained that the mean result of four tests on the same coal sample is correct to within ± 1 unit in 99 out of 100 cases and within $\pm 0{\cdot}5$ unit in 80 out of 100 cases; there is thus some assurance that different investigators can reproduce closely results on the same coal.

The Specification includes the method for the determination of the swelling number, the method of reporting and an appendix recording some of the main points studied during the standardisation of the test.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection and Determination of Diacetyl and Methyl-acetyl-carbinol in Bakery Products. H. Schmalfuss and H. Werner. (*Z. Unters. Lebensm.*, 1938, **76**, 113–118.)—In comparison with older methods, the method described below has the advantage that it is applicable to small amounts of material and may be used to study the distribution of diacetyl in the product. The apparatus consists of a rubber-stoppered, conical, 150-ml. flask with a delivery tube, 40-cm. long and 1·2 cm. internal diameter, bent sharply 5 cm. from the mouth of the flask and water-jacketed for 20 cm. of its length. The flask is heated by a Bunsen burner, but with large amounts of sample when there is danger of the charring of starchy matter on the sides a glycerin bath at 150° to 160° C. may be used. Into

* Obtainable from the Publications Department, 28, Victoria Street, London, S.W.1. Price 2s. net; post free 2s. 2d.

each of two test-tubes are put 0·05 ml. of 22·5 per cent. hydroxylamine hydrochloride solution, 0·05 ml. of 1·25 per cent. nickel sulphate ($NiSO_4.7H_2O$) solution and 0·1 ml. of 20 per cent. ammonia solution. The flask contains 20 ml. of saturated sodium chloride solution; this is distilled and 1 ml. of distillate is collected in each test-tube, the volume being measured by comparison with a similar tube containing 1·2 ml. of water. The contents of the tubes are made alkaline, if necessary, by the addition of 0·1-ml. portions of the ammonia solution and boiled until the volume in each tube (measured as before) is 1·05 ml. The contents of the tubes when cold should show no colour or at the most only a faint violet. The test is repeated with 20 ml. of saturated sodium chloride solution and 10 g. of the sample, finely powdered if solid or drawn out into narrow threads if dough-like. If the diacetyl-content is not less than 0·2 mg. per 100 g. a distinct red colour or crystalline deposit of nickel diacetyl-dioxime will appear in the first tube and, unless the amount of diacetyl present is too large, the liquid in the second tube will remain colourless. If no colour appears in the first tube a control test is made by introducing 0·50 ml. of 0·004 per cent. diacetyl solution into the flask and repeating the distillation. For the detection of methyl-acetyl-carbinol the test is made in the same way, but the sodium chloride solution is replaced by 50 per cent. ferric chloride solution. During the initial blank determination the source of heat should be adjusted so that the first drop distils after two minutes and no yellow colour should appear in the distillate. A control test may be made with 0·5 ml. of 0·004 per cent. methyl-acetyl-carbinol solution. For quantitative purposes the amount of the sample which gives the same colour as the control amount of 0·02 mg. is determined. If both diacetyl and methyl-acetyl-carbinol are present the amount of diacetyl found by the first procedure is deducted from the total diacetyl (which includes diacetyl produced by oxidation of methyl-acetyl-carbinol) found by the second procedure. The difference in the molecular weights of the two compounds may be neglected. A number of products were examined by this method. Three types of bread gave the following amounts of methyl-acetyl-carbinol (mg. per 100 gm.) in the crust and crumb respectively:—2·0, 0·67; 0·5, <0·13; 3·1, 0·4. No sample contained diacetyl and a sample of the cracker type (*Knäckebrot*) was free from methyl-acetyl carbinol. Two types of dough contained no diacetyl and 5·0 and 0·67 mg. of methyl-acetyl-carbinol respectively per 100 g. Contrary to the results of Vissert 't Hooft and de Leeuw (*Cereal Chem.*, 1935, **12**, 213) more methyl-acetyl-carbinol occurs in the crust than in the crumb. Apparently diacetyl plays no part in producing the odour and flavour of the kinds of bread investigated. A. O. J.

Composition of the Soya-bean in South Africa. N. J. Viljoen. (*Dept. Agric. and Forestry, Union of South Africa, Science Bull. No.* 169.)—About 16 varieties of soya-bean were analysed, and although the ash and fibre figures remained fairly constant for them all, oil and protein varied considerably, *viz.* from 15·4 to 21·3 per cent. for oil and from 37·5 to 42·0 per cent. for protein. When the same varieties were planted for three consecutive years on the same soil it was found that seasonal conditions had a pronounced effect; in some years there was a high development of oil and in others of protein. The quality of the oils, however,

appeared to be little affected by environment, and the expressed oils of 14 varieties were physically and chemically very similar. Mean values found were: n_D^{40}, 1·4675; saponification value, 198·0; iodine value, 129·5; Reichert–Meissl value, 0·25; Polenske value, 0·24. It was found that the later the beans are planted the lower the oil-content and the higher the protein, and the time required for the seed to reach maturity is also reduced, *e.g.* from 112 to 98 days. For practical purposes the fertility of the soil seems to make little difference, but climate has a marked influence. The Brownie variety, grown in different places in the Union, had an oil-content ranging from 12·3 to 21·3 per cent. and protein from 35·8 to 51·5; Yellow 1 grown at the same places showed a variation ranging from 12·2 to 22·1 for oil and from 32·6 to 48·1 for protein. Minimum temperature was found to be the chief factor concerned, and there is a positive correlation between the minimum temperature and percentage of oil, and a negative one between the minimum temperature and protein-content. There are also significant positive and negative correlations respectively between oil percentage and mean temperature, and protein percentage and mean temperature, but no correlation between maximum temperature or rainfall and percentages of oil and protein. The use of phosphate as fertiliser causes an increase in yield of beans over no fertiliser, and an increase in oil-content over that obtained with phosphorus and nitrogen in conjunction, and phosphorus and potassium in conjunction cause an increase in oil-content over that obtained with phosphorus and nitrogen together. Phosphorus and nitrogen together cause an increase in protein over phosphorus used alone, as do phosphorus and nitrogen together over phosphorus and potassium together, and nitrogen alone over phosphorus and potassium in conjunction. The best fertiliser treatment appears to be 200 to 500 lbs. of superphosphate per acre, double this amount giving no greater returns. A study of the inheritance of oil and protein in the soya-bean indicates that a raising of the oil-content may be possible by hybridisation, but a highly significant negative correlation exists between oil- and protein-contents. A unit rise in oil-content is associated with a fall of 2·03 per cent. in protein, and a unit rise in protein with a fall of 0·32 per cent. in the oil-content. Further, a significant negative correlation has been demonstrated between seed weight and oil-content, and a positive correlation between seed weight and protein-content. D. G. H.

Determination of Iron in Malt Beverages. P. P. Gray and I. M. Stone. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 415–417.)—Iron in beer may be determined rapidly—within 45 minutes—by a colorimetric method. A block comparator with 6 holes and test-tubes graduated at 10 ml. are used, the apparatus being similar to that used in *p*H determinations. *Reagents*: (*a*) *Standard iron solution.*—Two drops of hydrochloric acid are added to a freshly-prepared solution of 3·512 g. of ferrous ammonium sulphate hexahydrate in water, and the solution is made up to 500 ml. Ten ml. of this solution are then made up to 1 litre; 1 ml. of the diluted solution contains 0·01 mg. of iron. (*b*) *Sodium hydrosulphite solution.*—Approximately 2 per cent., freshly prepared and free from iron. (*c*) *αα′-Dipyridyl solution.*—Two ml. of dilute (1 : 2) acetic acid are added to 100 mg. of αα′-dipyridyl, and the mixture is diluted to 50 ml. with water. For permanent standards, 0·5 ml. of (*b*)

is added to a known volume of (*a*), and the volume is made up to 10 ml. with water; 0·5 ml. of (*c*) is then added to this.

Method.—Ten ml. of de-gassed beer are put into a comparator tube and treated with 0·5 ml. of (*c*). After mixing, the tube is heated for 30 minutes in a water-bath at 70° C. to develop the orange to orange-red colour. It is then viewed through a comparator tube containing 10 ml. of water, while duplicate comparison tubes are each viewed through 10 ml. of de-gassed untreated beer, in order to compensate for the beer colour. If corked and sealed with paraffin wax the permanent standards will keep for months in the dark. Addition of 5 p.p.m. of aluminium, chromium, cobalt, copper, lead, manganese, nickel, tin and zinc, respectively, to portions of each of three beers which contained (i) 1 p.p.m., (ii) 3 p.p.m., (iii) 5 p.p.m. of iron caused no interference with the colour. Analyses of various beers by this method gave results in agreement with those of either the Siebenberg–Hubbard ferrocyanide method (*cf. J. Assoc. Off. Agr. Chem.*, 1936, **19**, 489–493) or the thiocyanate method. Comparative experiments on the preliminary reduction of the beer with sodium hydrosulphite showed that this had no effect on the colour and indicated that all the iron was originally present in the ferrous state. Another reagent, 1: 10-phenanthroline, gives results similar to those obtained with $\alpha\alpha'$-dipyridyl, but is less sensitive because the colour is more orange; also, traces of cobalt, nickel and copper affect the test. Owing to the rapidity of the test, it may be used for the regular control of the amount of iron in beer in process, during storage and in the finished form. (Amounts only slightly above 0·5 p.p.m. have sometimes been found harmful to appearance, colour and taste.) E. B. D.

Gravimetric Determination of α-Hop Resin. G. Hagues and A. W. D. Hartley. (*J. Inst. Brewing*, 1938, **44**, 375–385.)—In investigating the Ford and Tait method and its modifications (Ford and Tait, *J. Inst. Brewing*, 1924, **30**, 426; Walker and Hastings, 1928, **34**, 9; Abst., ANALYST, 1928, **53**, 104; 1929, **35**, 229) for the determination of α-hop resin, difficulty was experienced in obtaining the end-point of the precipitation of the α-resin as the lead salt, and precipitation graphs were therefore plotted, showing as abscissae the quantities of lead acetate added and as ordinates the weights of precipitate obtained. It was found that true quantitative precipitation is not always obtained by the standard methods. The precipitation graph should consist of two lines, a rising straight line, OX, along the theoretical line, OA, and a falling line, almost straight, intersecting at the point X, which indicates complete precipitation of the resin. If no such break occurs precipitation is found not to be quantitative. When working with a new hop of the Saaz type this complete precipitation may be obtained by reducing the temperature of dissolution of the ether-extracted resins in methyl alcohol to 40° C., but with old English hops considerable errors are involved, and even when extraction with ether is made at low temperatures and the resins are dissolved and their solutions filtered at 0° C., the same quantitative exactness cannot be obtained as with a Saaz hop, although more nearly accurate figures are obtained by using these precautions. Slow precipitation, which is considerably affected by the concentration of the reacting substances, is indicative of a non-quantitative

reaction, and the rising straightline portion of the graph is then closer to the theoretical line at its higher stages than at its lower. Solvents other than ether were tried but with no advantage, nor did the use of other precipitants, such as lead chloroacetate, glycollate, propionate, lactate, benzene-sulphonate, etc., prove more satisfactory than the usual method, using lead acetate. D. G. H.

Factors influencing the Composition of the Depot Fat of Fishes. J. A. Lovern. (*Biochem. J.*, 1938, **32**, 1214–1224.)—The separate effects of diet, water temperature and salinity on the composition of the depot fat of fish have been investigated, eels being used as the experimental animal. In the first experiments three groups of eels of approximately the same length were confined in large tanks containing respectively fresh water at 14° C., fresh water at 23° C., and sea water at 23° C. The eels were fed for 6½ months on mussels; at the end of this time they were killed, and the body fats were extracted and examined. The fat of eels of the same size taken from the Dee estuary was also examined. The composition of the fats of each group is given in the following table, together with that of the mussels on which they were fed.

			Composition of fatty acids								
			Saturated Per Cent.			Unsaturated Per Cent.					
Group	Fat Per Cent.	Iodine value	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}
Eels											
Control	9·3	118·5	4·3	16·8	2·5	0·1	8·8 (−2·2H)	39·4 (−2·5H)	20·8 (−5·6H)	7·3 (−10·2H)	
Fresh water, 14° C.	18·0	119·1	3·3	20·5	2·7	0	11·6 (−2·4H)	39·4 (−2·7H)	16·1 (−6·3H)	6·4 (−10·0H)	
Fresh water, 23° C.	10·2	121·5	4·1	19·4	2·2	0	5·7 (−2·4H)	37·5 (−2·8H)	20·6 (−5·5H)	10·5 (−9·2H)	
Sea water, 23° C.	9·4	116·6	3·7	17·4	3·9	0	9·5 (−2·1H)	39·6 (−2·4H)	16·8 (−5·2H)	9·1 (−8·6H)	
Mussels											
Fat	1·1	—	1·9	16·7	1·7	0·3	10·6 (−2·5H)	21·5 (−4·1H)	29·9 (−7·3H)	13·9 (−9·3H)	3·5 (−?H)
Phosphatides		—	0	27·3	6·2	0	5·0 (−3·2H)	16·4 (−4·0H)	32·2 (−6·0H)	12·9 (−8·5H)	?

In a second experiment, larger eels were used. They were kept in tanks containing respectively sea water at 14° C., fresh water at 14° C., and fresh water at 23° C. The eels in the fresh-water tanks were fed on herrings; those in sea-water on mussels. The amount and composition of the fats of these eels and of controls, together with those of herring fat, were found to be:

			Composition of fatty acids							
			Saturated Per Cent.			Unsaturated Per Cent.				
Group	Fat Per Cent.	Iodine value	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}
Control	24·1	119·0	4·3	17·8	1·7	Trace	9·2 (−2·2H)	38·4 (−2·7H)	20·1 (−6·0H)	8·5 (−9·3H)
Sea water, 14° C. ..	16·6	114·1	4·8	17·6	2·6	—	9·4 (−2·2H)	41·6 (−2·4H)	16·4 (−5·8H)	7·6 (−9·1H)
Fresh water, 14° C.	20·6	140·4	6·4	17·1	1·3	—	6·9 (−2·4H)	31·9 (−3·0H)	22·2 (−5·4H)	14·2 (−7·5H)
Fresh water, 23° C.	23·9	137·6	6·0	16·5	1·1	0·6	8·3 (−2·2H)	33·9 (−2·8H)	22·6 (−5·5H)	11·0 (−7·0H)
Herring	20·7	—	8·3	12·1	0·3	0·5	6·4 (−3·4H)	21·0 (−4·5H)	28·3 (−5·5H)	23·1 (−4·6H)

The diets fed, mussels and herrings, represent the extremes of non-fatty and fatty food likely to be eaten by an eel, and the composition of the fat of each differs considerably from that of eel fat. The fatty acids of mussel fat contain much less C_{18} acids and less C_{14} and C_{22} acids than those of eel fat; whereas herring fat contains much more C_{22} acids and much less C_{18} acids than eel fat, as well as showing other differences. The depot fat of the eels fed on mussels was not appreciably modified in the direction of mussel fat, but the fat of the animals fed on herrings showed appreciable modification, and it has a composition corresponding with that of a 60 : 40 mixture of eel fat and herring fat. Calculation shows that a continual turnover between depot fat and ingested fat (as postulated by Schoenheimer and Rittenberg) would have given a 25 : 75 mixture of eel fat and herring fat, so that it seems unlikely that the ingested fat is deposited in the depots and a certain amount of the mixed fat withdrawn.

The only generalisation that can be made regarding the effect of temperature on the composition of the fat is that the fats deposited at the higher temperature are somewhat more saturated than those deposited at the lower temperature, but the effect is not very pronounced. Salinity had no effect on fat composition.

F. A. R.

Acidimetric Titration of Ergometrine. F. Reimers. (*Quart. J. Pharm.*, 1938, **11**, 252–259.)—In view of the variable amounts of solvent of crystallisation retained by different samples of ergometrine, a simple method of estimating the ergometrine-content of commercial samples is desirable. A volumetric method has been based on the observation that the electrometric titration curve showed a sharp inflection at *p*H 4·4, suggesting the use of bromophenol blue as indicator. On account of the high cost of ergometrine it was essential to use a minimum quantity of material, and a micro-method was accordingly devised. The ergometrine is mixed thoroughly and 5 to 10 mg. are weighed directly into a small test-tube and dissolved by warming in a quantity of 0·02 *N* hydrochloric acid equivalent to about 80 per cent. of that required for complete neutralisation; the acid is run in from a micro-burette (2 ml.). The solution is then cooled and a fraction of a drop of bromophenol blue solution is added. The titration is continued with 0·02 *N* hydrochloric acid until a bluish-green colour appears. The titration must be done in daylight; to avoid interference from the fluorescence of ergometrine the tube must be screened from direct illumination. In order to obtain a sufficiently distinct colour-change the quantity of acid added toward the end of the titration should not be less than 0·005 to 0·01 ml. at a time. The error so introduced is not greater than 0·5 per cent. F. A. R.

Determination of Stem in Ipecacuanha. A. W. Lupton. (*Quart. J. Pharm.*, 1938, **11**, 225–233.)—Commercial samples of whole ipecacuanha were separated by hand into stem and roots, and it was found that in only one sample out of eleven was the amount of stem present less than the official figure of 5 per cent. The rest contained from 9·3 to 24·2 per cent. The estimation of the amount of stem present in powdered ipecacuanha root is not easy. The only feature of the stem that enables it to be distinguished from the root in the powdered drug is the presence of sclerenchymatous cells of the pericyclic sclerenchyma.

These cells are pale yellow and brightly transparent after "crude fibre" treatment, and have thick walls with characteristic canals running outwards. They occur either as elongated rectangular cells, 85 to 120μ in length, and 20 to 25μ in width, or as square to triangular cells, 25 to 30μ by 50μ. They are easily distinguished from xylem elements, which they superficially resemble, because the xylem cells have thin walls and a characteristically pitted appearance. The following method of estimating the amount of stem in powdered ipecacuanha is recommended:—About 15 g. of the sample are passed through a No. 90 sieve, exactly 10 g. of the mixed powder are transferred to a porcelain dish together with 50 ml. of 10 per cent. nitric acid, and the suspension is boiled for half-a-minute. It is then filtered through a sintered glass funnel and washed with boiling distilled water. The residue is transferred to the dish, 50 ml. of 2·5 per cent. sodium hydroxide solution are added, and the suspension is boiled for half-a-minute, filtered and washed, first with hot 0·5 per cent. nitric acid, and then with hot water. The residue is mixed with a little suspending fluid (mucilage of tragacanth 1, glycerin 2, distilled water 1) containing 0·1 g. of lycopodium. Portions of the suspension are mixed on a microscope slide with sufficient suspending fluid to give a reasonable count. The lycopodium spores and the sclerenchymatous cells in the area represented by the diameter of the low-power microscope field and the length of the cover-slip are then counted. By this method it was found that 1 mg. of stem gives 33 sclerenchymatous cells, and by using this factor and the number of spores in 1 mg. of lycopodium (94,000) the weight of stem present in an unknown sample can readily be calculated from the cell count. By means of this technique as little as 2 per cent. of stem can be estimated with a fair degree of accuracy. F. A. R.

Identification of Ecgonine, $C_9H_{15}NO_3$. F. Amelink. (*Pharm. Weekblad*, 1938, **75**, 861–864.)—Crystalline ecgonine containing 1 mol. of water of crystallisation has m.p. 198° C. (205° C. in the anhydrous state) and amphoteric properties; its solubility in water is 1 : 5, the solution being neutral to methyl red. It cannot be removed by extraction with ether, and amyl alcohol effects only a partial removal. The following tests (which are illustrated by sketches of the crystals produced) are carried out with drops of a 1 per cent. solution of the sample in water or in 0·5 *N* hydrochloric acid:—(1) A drop of platinic chloride solution produces no precipitate with a drop of either solution, but the subsequent addition of a saturated solution of sodium iodide produces black, rectangular prisms of ecgonine iodoplatinate, 10 to 40μ in size (sensitiveness, 0·1 per cent. for the acid solution). If the test is made by adding the sample in the solid state to a dilute solution of the iodide containing only a little platinic chloride, the crystals are 50μ in size; they are produced more rapidly, and the surrounding liquid is lighter in colour. After about 10 minutes a few diamond-shaped hexagonal prisms form and these provide a means of distinguishing ecgonine from betaine, which in other respects behaves similarly. Other points of difference, however, are the less geometrical outline and size of the ecgonine crystals (100μ), their green shade when viewed in reflected light, and the colourless surrounding liquid. (2) If the procedure described above is followed with gold chloride and sodium bromide, 4-sided (usually rectangular) ruby red to brown, weakly anisotropic dichroic crystals

of ecgonine bromo-aurate are obtained from both solutions on warming (size, 5 to 15μ; sensitiveness, 0·2 per cent.). On standing, smaller prisms develop; these are more strongly doubly-refracting, and are *d*-rotatory; sometimes they are deformed or aggregated in cross- or star-shaped clusters. Betaine gives similar results, but the crystals are always strongly doubly-refracting. (3) Mercuric chloride produces (especially in the acid solution) square-shaped aggregates of ill-defined, rectangular, weakly anisotropic scaly crystals of the chloromercurate, 25 to 80μ in size. The test may be carried out in the cold or with the solid reagent, and under similar conditions betaine produces strongly anisotropic, ill-defined pyramids. (4) The hydroxide, ferrocyanide or ferricyanide of potassium gives no reaction with either solution. (5) Dragendorff's reagent produces a brown precipitate, although when the test is carried out in warm acid solution, brown or black hexagonal plates, 5 to 30μ in size, are obtained; as a rule, these are not doubly-refracting (sensitiveness, 0·2 per cent.); solutions in water give only oily drops. A few strongly doubly-refracting, *d*-rotatory hexagonal prisms, 130μ in size, are also obtained. Betaine gives similar results. (6) If the sample is warmed with picrolonic acid and a drop of 90 (vol.) per cent. alcohol is added, a crystalline precipitate is produced which is neither particularly characteristic nor well-defined; however, it differs sufficiently from that produced with betaine to enable the two substances to be distinguished from one another. J. G.

Identification of *p*-Aminobenzenesulphonamide (Sulphanilamide, "Prontosil Album," etc.). F. Amelink. (*Pharm. Weekblad*, 1938, **75**, 851–853.)—Van Zyp's crystallographic methods (ANALYST, 1938, 511) are unsuitable for routine chemical work, and the following tests are recommended:—(1) If a splinter of wood (*e.g.* from a match-box) is soaked in an acid solution of the sample, an orange-yellow colour, which is destroyed by the action of ammonia, indicates the presence of sulphanilamide. This serves only as a preliminary sorting test, since it is also given by sulphanilic acid. (2) Addition of platinic chloride in the presence of 0·5 *N* hydrochloric acid, followed by warming and scratching the walls of the containing-vessel or the microscope slide, produces light yellow convex lens-shaped crystals of the chloroplatinate; these are 30 to 250μ in length, and are *l*-rotatory and very soluble. (3) If a warm saturated solution of sodium bromide is then also added, orange-yellow hexagonal prisms of the bromoplatinate, 15 to 70μ in length, are produced. These grow on standing, are *d*-rotatory, and are produced from solutions stronger than 0·2 per cent. (4) A cold saturated solution of picric acid in water precipitates large yellow needles or prisms, frequently as star-shaped aggregates, which grow on standing. They are strongly double-refracting and produce complete extinction, and they are detectable with 0·5 per cent. solutions. (5) If a solution of sulphanilamide is warmed with a neutral solution of picrolonic acid, the containing vessel being scratched, sheafs or star-shaped clusters of light-yellow lens-shaped needles, or prisms with rounded outlines, are produced; these are 130μ in length and are strongly double-refracting and often *l*-rotatory, although sometimes *d*-rotatory. The limiting dilution is 0·5 per cent. These four reactions (2 to 5) are not given by sulphanilic acid. (6) A 0·1 per cent. solution of sulphanilamide produces with 1 drop of bromine water in acid solution

a precipitate of small needles, which are frequently curved, and under high magnifications have the appearance of leaf-shaped prisms. They are 30 to 50μ in length and weakly double-refracting; they are also produced by sulphanilic acid, although their structure is then less well-defined. The crystalline structures described are all illustrated by drawings. J.G.

Biochemical

Stable Nitroprusside Solution for Acetone Bodies in Urine. J. Ingham (*British Med. J.*, Aug. 13th, 1938, 348.)—An aqueous solution of sodium nitroprusside can be rendered quite stable by the addition of a little conc. nitric acid, which in no way interferes with the reaction for acetone bodies in urine. The reagent is preferably made in two solutions:—I. A mixture of 200 ml. of a saturated solution of ammonium sulphate with 200 ml. of ammonia solution (sp.gr. 0·88). II. Ten g. of sodium nitro-prusside crystals dissolved in 99 ml. of water and treated with 1 ml. of conc. nitric acid. In applying the test 5 ml. of the urine are mixed with 5 ml. of Solution I, 1 ml. of Solution II is added, and the test-tube is allowed to stand for a minute. In the presence of 0·1 per cent. or more of acetone bodies a deep purple colour will be produced, whilst if only a trace is present the colour will be deep red.

Enzymatic Digestion of Wool. J. I. Routh and H. B. Lewis. (*J. Biol. Chem.*, 1938, **124**, 725–732.)—Extracted washed wool, freed from fat, was very slowly attacked by trypsin, the hydrolysis amounting to 5 to 7 per cent. at the end of 30 days. After the wool so treated had been ground in a ball mill for a prolonged period it was found to contain a notably higher proportion of ash and a lower proportion of cystine. The powdered wool yielded a water-soluble fraction containing nitrogen and sulphur, which was not attacked by trypsin. It is possible that prolonged grinding might have brought about a change in the cystine molecule to give a product no longer reactive to the colour tests used, and oxidation of part of the cystine might account for the appearance of inorganic sulphate in the aqueous extract. The powdered wool and the material left after extraction with water were readily attacked by trypsin and pepsin. Kerateins produced by the reducing action of alkaline thioglycollate solutions on wool were hydrolysed more extensively and much more rapidly by pepsin and trypsin than were the proteins of powdered wool. D. G. H.

Precise Method for the Determination of Carotene in Forage. D. W. Bolin and A. M. Khalapur. (*Ind. Eng. Chem. Anal. Ed.*, 1938, **10**, 417–418.)—A sample of the material (5 to 10 g.) is refluxed for 40 minutes with 200 ml. of 95 to 97 per cent. ethyl alcohol, the extract is filtered hot, and the residue is washed with hot alcohol (about 150 ml.). The alcoholic filtrate is diluted to a volume of 400 ml., half of it is transferred to a 250-ml. flask, and 25 ml. of 10 per cent. alcoholic potash are added. The solution is shaken and allowed to stand for 2 hours or, alternatively, heated for half-an-hour in a water-bath at 80° C. It is then cooled and made up to volume, and 25 ml. are transferred to a separating funnel. About 15 ml. of petroleum spirit and 7 ml. of water are added, and the

solution is shaken. The lower layer is run off and extracted twice more with petroleum spirit (10 ml.). The combined extracts are washed with water until free from alkali, and then extracted with 25-ml. portions of 85 per cent. methyl alcohol until the alcohol is colourless. The petroleum solution is extracted twice more with 90 per cent. methyl alcohol and then filtered through anhydrous sodium sulphate into a 50-ml. flask and made up to volume. The carotene-content is determined spectrophotometrically or by comparison with the standard dye solution described by Guilbert (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 452). The method as described gives better recovery of carotene than Guilbert's method.

F. A. R.

Vitamin A and Carotenoids. Kinetic Study of the Carr–Price Reaction. P. Meunier and Y. Raoul. (*Compt. rend.*, 1938, **206**, 1148–1150.)—The Carr–Price reaction was studied kinetically with the aid of Meunier's electrophotometer (*Bull. Soc. Chim. Biol.*, 1937, **19**, 113). When a chloroform solution of antimony trichloride only was added to solutions of vitamin A or carotene, the rate at which the resulting blue colour faded was about the same with both compounds. If, however, at the moment of adding the antimony trichloride solution, two drops of acetic anhydride were also added, a pronounced difference in the stability of the two colours was observed. The blue colour with β-carotene showed no decrease in intensity, whereas that with vitamin A faded very rapidly. The addition of antimony trichloride solution to the unsaponifiable matter of fresh-water fish liver oils resulted in the formation of a green, not a blue, colour corresponding with the absorption band at 693$m\mu$ characteristic of vitamin A_2. This colour also faded, but much less rapidly than that of vitamin A_1. It is claimed that the rate of fading of the colours formed in the presence of acetic anhydride is characteristic, and that β-carotene, vitamin A_1 and vitamin A_2 can be distinguished from one another by this means.

F. A. R.

Physico-chemical and Biochemical Study of Vitamin A_2. E. Lederer and F. H. Rathmann. (*Biochem. J.*, 1938, **32**, 1252–1261.)—Vitamin A_2, the analogue of vitamin A that gives on addition of antimony trichloride solution an absorption band with a maximum at 693$m\mu$, has now been shown to give a second band at 650$m\mu$. This band is usually masked by the stronger band at 693$m\mu$, but it can be rendered visible by adding to the solution the fatty acid fraction from freshwater fish liver oils; these acids diminish the absorption at 693$m\mu$ but not at 650$m\mu$. The band at 640 or 645$m\mu$ observed in some natural oils may be due to vitamin A_2; after saponification the fatty acid inhibitor is removed and the 645$m\mu$ band then becomes masked by the more intense 693$m\mu$ band. The assumption previously made that $E^{1\%}_{1\,cm.}$ 693$m\mu$ for vitamin A_2 and $E^{1\%}_{1\,cm.}$ 620$m\mu$ for vitamin A, are both equal to about 5000 is now shown to be true, but a second assumption that in a mixture of the two vitamins, the absorption at 620$m\mu$ is solely due to vitamin A_1, is shown to be untrue. In concentrates rich in vitamin A_2 where $E^{1\%}_{1\,cm.}$ 693$m\mu$/$E^{1\%}_{1\,cm.}$ 620$m\mu$ = 3, nearly half the absorption at 620$m\mu$ is due to vitamin A_2. $E^{1\%}_{1\,cm.}$ 695$m\mu$/$E^{1\%}_{1\,cm.}$ 620$m\mu$ for pure vitamin A_2 lies between 6 and 8. This observation necessitates a re-evaluation of the biological activity

of vitamin A_2 concentrates, for these contain much less vitamin A_1 than was thought to be the case. The purest concentrates prepared, which are completely soluble in 77 per cent. alcohol, possess ultra-violet absorption spectra with bands at 345 and 280$m\mu$. The relative quantities of vitamins A_1 and A_2 expressed by the ratio $E^{1\%}_{1\,cm.}$ 693$m\mu$/$E^{1\%}_{1\,cm.}$ 620$m\mu$ were measured for concentrates prepared from the liver oils of freshwater fish from several countries of Europe; the ratio was more or less constant for a given species. Pike-perch (*Lucioperca lucioperca*) pike (*Esox lucius*), catfish (*Silurus glanis*) and perch (*Perca fluviatilis*) had ratios of 2·0 to 2·7; trout (*Salmo irideus*), carp (*Cyprinus carpio*), sturgeon (*Acipenser sturio*) and salmon (*Salmo salar*) had lower ratios (0·4 to 0·8). Marine fish (*Gadus merlangus, Hippoglossus hippoglossus, Ishinagi sterelepis*) and land animals such as sheep, chicken and frog (*Rana esculenta*) had still lower ratios (0·03 to 0·27). In most freshwater fishes $E^{1\%}_{1\,cm.}$ 693$m\mu$/$E^{1\%}_{1\,cm.}$ 620$m\mu$ was lower for the intestinal oils than for the liver oils, but in the carp the reverse was observed. A more detailed investigation was made of the distribution of vitamins A_1 and A_2 in the intestinal tract of the pike-perch. For the stomach and the fat surrounding the caeca and incidentally for the food, *i.e.* the stomach contents, the ratio was 1, but for the pyloric caeca itself the ratio was 2·4. The absence of vitamin A_2 from mammalian livers is the result of its absence from the food, for the administration of a vitamin A_2 concentrate to both rats and frogs increased the ratio $E^{1\%}_{1\,cm.}$ 693$m\mu$/$E^{1\%}_{1\,cm.}$ 620$m\mu$ of the liver fat. F. A. R.

Ascorbic Acid and Phosphatase Activity. E. J. King and G. E. Delory. (*Biochem. J.*, 1938, **32**, 1157–1162.)—A claim made by Thannhauser, Reichel and Grattan (*J. Biol. Chem.*, 1937, **121**, 697) that ascorbic acid is an intense activator of serum phosphatase has been shown to be unfounded. [Thannauser *et al.* acknowledge their error in a paper which follows that of King and Delory.—*Abstractor.*] The investigation involved the estimation of phosphorus in the presence of ascorbic acid. Since the latter reduces the phosphomolybdic acid formed in the method of Briggs (*J. Biol. Chem.*, 1922, **53**, 13), this method could not be used. The method of Ammon and Hinsberg (*Z. physiol. Chem.*, 1936, **239**, 207; *cf.* ANALYST, 1936, **61**, 428), in which ascorbic acid is used as the reducing agent, was satisfactory. A new procedure was also devised, in which phosphorus is removed from the solution containing the interfering substances by precipitation as calcium phosphate, the precipitation being rendered complete by entrainment with light magnesium carbonate powder. Measured amounts of phosphate solution are introduced into centrifuge tubes, and the solutions are neutralised (if necessary) to phenolphthalein by addition of conc. ammonia solution; exactly 0·2 ml. in excess is then added. One ml. of 2·5 per cent. calcium chloride solution and 1 ml. of a 0·5 per cent. suspension of "light" magnesium carbonate in water are added, and the tubes are shaken and allowed to stand for 30 minutes. They are again shaken and centrifuged, and the supernatant liquids are decanted and discarded. The precipitates are washed with 5 ml. of 2 per cent. ammonia solution saturated with calcium phosphate and then dissolved in 1·1 ml. of 60 per cent. perchloric acid. About 10 ml. of water are added, followed by 1 ml. of 5 per cent. ammonium molybdate solution and 0·5 ml. of 1:2:4-aminonaphtholsulphonic

acid solution. The mixture is diluted to 15 ml. and, after standing for 10 minutes, the blue solutions are compared with standard solutions in a colorimeter. When only small amounts of phosphate are present, the precipitate is dissolved in 0·25 ml. of perchloric acid followed by 2·5 ml. of water, 0·2 ml. of ammonium molybdate solution and 0·1 ml. of aminonaphtholsulphonic acid solution, making a total volume of 3 ml. The recovery of inorganic phosphate (mg. of P) from solutions containing various interfering substances is recorded in the following table:

(1)	Phosphate precipitated from simple solution:				
	P present	0·025	0·050	0·075	0·100
	P recovered	0·025	0·048	0·080	0·100
(2)	Phosphate precipitated from 2·5 per cent. trichloroacetic acid solution:				
	P present	0·010	0·020	0·030	0·040
	P recovered	0·010	0·018	0·026	0·037
(3)	Phosphate precipitated from solution containing 5 mg. of ascorbic acid:				
	P present	0·010	0·050	0·070	0·100
	P recovered	0·010	0·048	0·067	0·096
(4)	Phosphate precipitated from 2·5 per cent. trichloroacetic acid solution containing 5 mg. of ascorbic acid:				
	P present	0·020	0·050	0·070	0·100
	P recovered	0·018	0·050	0·071	0·100
(5)	Phosphate precipitated from a solution containing 5 mg. of ascorbic acid, trichloroacetic acid and 1 ml. of 5 per cent. sodium β-glycerophosphate solution:				
	P present	0·020	0·050	0·070	0·100
	P recovered	0·020	0·049	0·070	0·099

F. A. R.

Determination of Vitamin C in Milk. B. Willberg. (*Z. Unters. Lebensm.*, 1938, **76**, 128–132.)—Unless special precautions are taken, the determination of vitamin C in milk by titration with 2 : 6-dichlorophenol-indophenol solution is affected by atmospheric oxidation. Radeff (*Milchwirtsch. Forsch.*, 1937, **19**, No. 3) has described a method by which sera stable with respect to vitamin C are obtained, the coagulant being sulphosalicylic acid. Ascorbic acid, although unstable in aqueous solution, is stable in solutions containing certain organic acids. Milk sera prepared by coagulation with oxalic acid and saturated sodium chloride solution (which assists clarification) are stable when kept in the dark or in diffused daylight, are practically unaffected by atmospheric oxygen, and may be titrated with the dye solution to the red end-point without the addition of a buffer. A 0·001 *N* solution of 2 : 6-dichlorophenol-indophenol is prepared by grinding 140 mg. of the dye in a mortar with successive amounts of water until solution is complete and diluting to 500 ml. It may be standardised with 0·001 *N* ascorbic acid solution (22 mg. dissolved in 250 ml. of water containing 10 ml. of saturated oxalic acid solution); this may be used unbuffered or after the addition of 7·5 ml. of saturated sodium acetate solution and is controlled by titration with 0·01 *N* iodine solution. Ferrous ammonium sulphate (0·001 *N*) may also be used for standardisation. The milk (50 ml.) is curdled with 4 ml. of saturated oxalic acid solution, and 10 ml. of saturated sodium chloride solution

are added. The filtered serum (25 ml.) is titrated with 0·001 *N* 2 : 6-dichlorophenol-indophenol solution to the red end-point or, after the addition of 7·5 ml. of saturated sodium acetate solution, to the blue end-point. The number of ml. of dye solution used, when multiplied by 2·4, gives the number required by 50 ml. of milk, a correction for the volume of curd being included in the factor. Each ml. of the dye solution is equivalent to 0·088 mg. of ascorbic acid. The serum prepared in this way has a titratable acidity of about 0·08 *N* and a *p*H of 2·7. A. O. J.

Vitamin C Content of some Germinated Cereals and Pulses. M. N. Rudra. (*J. Indian Chem. Soc.*, 1938, **15**, 191–193.)—A weighed amount of the grains to be tested was washed and soaked in tap-water for 24 hours, the water was drained away and the swollen grains were allowed to germinate. After 2 to 5 days' germination (calculated from the beginning of the soaking period) the grains were extracted with 20 per cent. trichloroacetic acid solution. A current of hydrogen sulphide was passed through the extract for 15 minutes, and the saturated solution was allowed to stand in the dark for 24 hours. It was then filtered, and a current of carbon dioxide was passed through the filtrate until it was free from hydrogen sulphide, after which it was titrated against 2: 6-dichlorophenolindophenol. The vitamin C content was calculated on the original dry weight of the grains, and the results obtained are given in the following table:

Grain	Period of germination (days)	Length of radicles (mm.)	Vitamin C content (mg. per 100 g.)
Barley (*Hordeum vulgare*) ..	3	2 to 4	19·5
,, ,, ..	5	6 ,, 10	31·1
Wheat (*Triticum vulgare*) ..	3	1 ,, 5	17·3
,, ,, ..	5	8 ,, 16	34·5
Bengal gram (*Cicer arietinum*) ..	2	2·5 to 5	40·7
,, ,, ..	3	5 ,, 15	44·9
,, ,, ..	4	10 ,, 20	50·6
,, ,, ..	5	15 ,, 25	68·5
Mung (*Phaseolus mungo*) ..	2	4 ,, 7	89·9
,, ,, ..	3	6 ,, 14	123·5
,, ,, ..	5	15 ,, 22	231·0

A commercial malt extract was found to contain 22·3 mg. of vitamin C per 100 g. F. A. R.

Vitamin C in Marine Algae. G. Lunde and J. Lie. (*Z. physiol. Chem.*, 1938, **254**, 227–240.)—The vitamin C contents of a number of marine algae were measured both by titration with 2 : 6-dichlorophenolindophenol and biologically. Good agreement was obtained between the two methods, except with the red alga *Rhodymenia palmata*; by biological assay it was found to contain only one-tenth of the amount of vitamin C estimated by titration. The green alga *Ulva lactuca* contained 27 mg. per 100 g. of dry substance. Of the brown algae, *Laminaria* species were found to contain 4 mg. per 100 g. in winter, and 10 to 46 mg. in spring; *Fucus* species 20 to 60 mg. per 100 g., with one value of over 100 mg. The red algae *Gigartina mamillosa* and *Porphyra umbilicalis* were very rich in vitamin C,

especially the latter, which was found to contain up to 140 mg. per 100 g. *Rhodymenia palmata*, on the other hand, contained only 5 mg. per 100 g. when tested biologically. F. A. R.

Relation between Vitamin C and Plant Phosphatase. K. V. Giri. (*Z. physiol. Chem.*, 1938, **254**, 126–138.)—Vitamin C alone had no effect on the hydrolysis of sodium glycerophosphate or sodium pyrophosphate by a phosphatase preparation made from soya-bean embryo. When traces of copper were present, however, the rate of hydrolysis was reduced by an amount depending on the amount of copper added. The hydrolysis of pyrophosphate was less affected by copper than that of glycerophosphate, and this was undoubtedly due to the protection against catalytic oxidation afforded to the vitamin C by the pyrophosphate. Glutathione, cysteine, cystine, hydrogen sulphide, potassium cyanide and sodium hydrosulphite behaved like pyrophosphate in preventing, wholly or partly, the inhibition of phosphatase activity by the copper-vitamin C system; like pyrophosphate they protected vitamin C from oxidation by copper. Potassium ferricyanide added to the phosphatase-vitamin C system reduced the rate of hydrolysis, but to a less extent than did copper. Methylene blue and the ascorbic acid oxidase of *Cucumis sativus* were without effect on the hydrolysis; so were dehydroascorbic acid and copper. The regulation of phosphate metabolism in plants therefore may possibly be brought about by interaction between phosphatase, vitamin C and glutathione. F. A. R.

Vitamin C Content of South African Oranges. P. J. Hamersma. (*Dept. Agric. and Forestry, Union of South Africa, Science Bull. No.* 163.)—Valencia, navel and seedling oranges from various districts in South Africa were stored at 38° C. for 3 months and longer. Values for vitamin C averaged about 0·5 to 0·6 mg. per ml. of juice, and no loss in vitamin occurred over the storage time; with seedlings the vitamin value increased. With some oranges the vitamin value was slightly lower in second-crop oranges. Although South African oranges are remarkably sweet, this fact was not found to affect the vitamin value. The loss of weight of oranges in cold store as a factor influencing the vitamin C content was found to be negligible, averages for 3 months being 3·6, 4·5 and 4·6 per cent. The loss of weight occurs in both peel and juice, but to a somewhat greater extent in the juice. Even if the whole loss in 12 weeks at 38° C. is ascribed to juice and the very high figure of 7·2 per cent. is taken (the total average juice-content of an orange being 72 ml. and the vitamin content 0·62 mg. per ml. or 44·6 mg. per orange), this figure will diminish only to 41·4 mg. during storage. No difference in acidity or vitamin-content per ml. was found between the navel and stem halves of oranges. The differences in vitamin C per ml. found between oranges of different trees, and still more of different localities, corresponded with differences in acidity, the correlation coefficient between these two factors for individual trees being 0·75. Variation in acidity may be accounted for by the amount of sun reaching the fruit, differences in fertiliser applications, amount of water received and general cultivation. D. G. H.

Bacteriological

Oxidation of Glucose by *Acetobacter suboxidans*. A. J. Kluyver and A. G. J. Boezaardt. (*Rec. Trav. chim. Pays-Bas*, 1938, **57**, 609–615.)—Recently it has been shown by Butlin that under certain conditions the acetic acid bacterium *Acetobacter suboxidans*, well known for its merely de-hydrogenating action on sugars and poly-alcohols, can also attack glucose with production of carbon dioxide. The observations of Butlin have been corroborated by the authors and the factors determining the divergent behaviour of the bacterium towards glucose are discussed. In addition, the authors record experiments proving that under certain conditions the bacterium converts glucose and gluconic acid into 5-ketogluconic acid almost quantitatively. In the first series of experiments 4-day old cultures were used, and in practically every instance the gaseous metabolism was found to be restricted to an oxygen consumption; when, however, 1-day or 2-day old cultures were used, production of carbon dioxide was observed. The capacity to produce carbon dioxide was, in the authors' experiments, retained for little longer than 2 days, but in Butlin's experience it was retained for 7 to 11 days. This is accounted for by the difference in the culture media employed, the authors using wort agar whilst Butlin used maize wort agar, the more vigorous growth in the former causing more rapid physiological ageing of the cells. This interesting bacterium, *Acetobacter suboxidans*, was found by Kluyver and Leeuw about fifteen years ago in Dutch beers, in which it has since been frequently encountered. Its application in the preparation of the incomplete oxidation products of sugars and alcohols offers many advantages over the use of Bertrand's *Acetobacter xylinum*; a plentiful supply of air to the latter brings about complete oxidation to carbon dioxide, whilst with the former, under ordinary working conditions, the restricted oxidative activity is maintained even under conditions of plentiful aeration. By the use of this micro-organism it has been found possible to shorten considerably the duration of the biochemical oxidation of sugars for the industrial manufacture of incomplete oxidation products. D. R. W.

Toxicological and Forensic

Toxicological Detection of Thallium. H. Kluge. (*Z. Unters. Lebensm.*, 1938, **76**, 156–159.)—A new method for the detection and determination of thallium in toxicological material depends upon its conversion into thallic chloride ($TlCl_3$ or $TlHCl_4$), which can be extracted from aqueous solution with ether (Shaw, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 93; Abst., ANALYST, 1933, **58**, 358). Thallous iodide is precipitated from the extract and determined gravimetrically or colorimetrically. A portion of the material not exceeding 70 g. is decomposed by treatment with hydrochloric acid and potassium chlorate, and, when decomposition is complete, the liquid is washed through a glass-wool filter with hot water and the filtrate is made up to 100 ml. or 250 ml. and filtered. An aliquot portion (90 per cent.) of the filtrate is shaken with ether until a colourless extract is obtained. The aqueous liquid is treated with chlorine and re-extracted with ether. The residue left after evaporation of the combined ethereal extracts is treated with nitric acid

and hydrogen peroxide until organic matter is destroyed, evaporated almost to dryness, and dissolved in water, and the solution is concentrated on the water-bath to a small volume (0·5 ml. for small amounts of thallium). The solution is then made slightly alkaline with 25 per cent. ammonia solution and heated with excess of 20 per cent. potassium iodide solution. The precipitate of thallous iodide is allowed to stand overnight and collected in a Gooch crucible, the filtrate being used to transfer the last portion. The precipitate is washed once with water and then with alcohol, and dried at 100° C. and weighed (Factor TlI to Tl = 0·6169). For an amount of thallium of the order of 1 mg. colorimetric determination is preferable. The precipitation of thallous iodide is carried out in a centrifuge tube, in which it is washed by centrifuging with alcohol until free from potassium iodide. It is then treated with 1 or 2 drops of conc. sulphuric acid and, when decomposition is complete, with 1 ml. of water, 1 to 3 drops of 10 per cent. sodium nitrite solution and 0·5 ml. of chloroform. After vigorous shaking, the chloroform layer is allowed to separate and is compared colorimetrically with equal volumes of chloroform containing known amounts of iodine. A series of standards may be prepared by precipitation of thallous iodide from a solution of thallium sulphate containing 1 mg. of thallium per ml. or a solution of potassium iodide (0·8123 g. per litre; 1 ml. = 1 mg. Tl) may be treated with sulphuric acid, sodium nitrite and chloroform. The ratio of 1 ml. of aqueous liquid to 0·5 ml. of chloroform should be maintained in all comparison tubes. The limit of the colorimetric method is 0·05 mg. of thallium. The precipitated thallous iodide may be examined spectroscopically. Control experiments indicated that the method has an accuracy of 99 per cent. The distribution of thallium in the organs of a young dog (weighing 3·77 kg.) poisoned with 1 g. of thallium sulphate (= 0·81 g. of thallium) was investigated. Of the amount administered about 15 hours before death, 38·52 per cent. was located. The percentage distribution of this amount was as follows:—stomach, 75·88; intestines, 14·25; liver, 5·32; lungs, 2·49; kidneys, 1·62; spleen, 0·27; heart and heart-blood, 0·18. A. O. J.

Lead Content of Human Blood. C. E. Willoughby and E. S. Wilkins, Jr. (*J. Biol. Chem.*, 1938, **124**, 639–657.)—The method used for finding the lead content of the blood was the dithizone method described by the authors previously (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 33, 285) with the following modifications. After complete solution of the digestion residue by the chloride and hydrochloric acid reagent, ammonium hydroxide (sp.gr. 0·90) is added rapidly until precipitation of the ferric hydroxide is complete, after which the excess is boiled off and the precipitate is immediately dissolved by the addition of 5 ml. of 4 per cent. citric acid solution to the mixture. The liquid is then partly neutralised by adding about 6 drops of ammonium hydroxide before the addition of the potassium cyanide. Later, and only when blood specimens are being examined, the lead dithizone complex, resulting from the initial lead separation, is not washed with dilute potassium cyanide before conversion into lead nitrate. It is shaken with 20 ml. of 1 per cent. nitric acid instead of being extracted twice with 10-ml. portions of acid. The optimum *p*H for the final extraction of the lead nitrate solution has been found to be 7·5 to 8·3.

Analyses were made of blood specimens from 189 individuals, in none of whom was any prior undue exposure to lead reported, and none of whom showed any signs or symptoms of lead poisoning; the proportion of lead found varied from 0·0 to 0·09 mg. per 100 g. of blood, with a most probable value of 0·025 ± 0·012 mg. of lead, which is significantly lower than found by most previous investigators. This may be accounted for by the methods and techniques used by the various workers, by geographical location or possibly, but not probably, by the fact that the individuals now tested were not in normal health when samples were taken. Of the 189 specimens analysed, 58 were separated into serum and cells and fibrin for individual analyses of these fractions, and approximately 90 per cent. of the serum samples contained no detectable amount of lead. It is concluded that 0·09, and even 0·10 mg., of lead may occasionally occur without indisputable clinical evidences of plumbism being present. D. G. H.

Acetone Chlorohaemin in Blood Testing. A. F. Richter and M. Hofman. (*Z. anal. Chem.*, 1938, **113**, 334–339.)—In Wagenaar's adaptation (ANALYST, 1936, **61**, 268) of Nencki and Zaleski's reaction (*Z. physiol. Chem.*, 1900, **30**, 384) for blood, which is based on the formation of crystals of "acetone-haemin," the addition of a mineral acid, and in particular of hydrochloric acid, is specified. It is now pointed out that the substance formed is acetone chlorohaemin, $C_{34}H_{32}N_4O_4FeCl.CH_3COCH_3$, and that the reaction can be produced by crystallisation of an extract in acetone and oxalic acid of the blood coagulum (*cf.* Hamsík, *id.*, 1930, **190**, 199) without addition of a mineral acid. Since the use of perchloric acid produces crystals, which according to analyses and qualitative tests contain no ClO_4-radical, it is believed that the nature of the acid added is irrelevant so long as Cl′-ions are present in the blood. It was not possible to produce an analogous iodine compound. Mineral acid aids the transformation from the α- to the β-structure (the Teichmann transformation) on heating, but the authors disagree with Wagenaar's conclusion (*Z. anal. Chem.*, 1930, **79**, 110) that this occurs when the acetone chlorohaemin is heated at 105° C. for 2 hours. They removed lipoids from this substance by extraction with petroleum spirit, and raised its temperature from 28° to 192° C. in 6 hours, and then maintained it at 192° C. for 1 hour. The Hamsík reagent for α-structure (*Pub. Fac. Med. Univ. Masaryk*, 1923, **2**, 1), *i.e.* a 5 per cent. solution of potassium hydroxide in methyl alcohol, then gave a positive result, and this reaction is suggested as preferable to the Teichmann reaction as a test for blood. The resulting crystals (which are illustrated) form characteristic star-shaped groups of needles, and after recrystallisation appear as opaque rosette-shaped clusters. Addition of imidazole produces ruby-red crystals of an addition compound (Hamsík, *Z. physiol. Chem.*, 1936, **241**, 156). On the other hand, the Wagenaar–Teichmann reaction gives crystals of chlorohaemin, which have the β-structure and are less characteristic, being opaque acorn-shaped groups consisting largely of 6-sided crystals with irregular outlines. In further experiments the acetone chlorohaemin was heated in 30 minutes to 250° and 280° C. (*cf.* Wagenaar, *loc. cit.*). When the temperature was maintained at 250° C. for 40 minutes, the Hamsík reaction was negative, and Wagenaar's test gave a doubtful result. It is concluded that the temperature of

250° C., suggested by Wagenaar, is too high, and that 240° C. is the maximum temperature for the Hamsík reaction. The haemochromogen reaction cannot be used as an indication of structure, since it is also given by β-haemin. J. G.

Agricultural

Comparison of Rapid Tests for Soil Nutrients with Laboratory Analyses. G. Griffith. (*J. Soc. Chem. Ind.*, 1938, **57**, 211–212.)—The results obtained by rapid analyses and by laboratory methods were compared for more than 70 samples. Available phosphate, potash, and calcium were determined by laboratory methods, 0·5 *N* acetic acid being used as the extracting agent. The rapid tests were identical in principle with the laboratory methods. A level teaspoonful of the soil was shaken for 1 minute with 10 ml. of water to which 5 drops of dilute (1 : 1) acetic acid had been added, and 1 ml. of the filtered extract was used for the tests for each of the nutrients. These tests were carried out as described by Spurway (*Michigan State Univ. Tech. Bull.* No. 132, 1926), except that assessment of colour or precipitate was made on a decimal scale. The following results were obtained:

Assessment by rapid tests		Mean results					
		0	1	2	3	4	5
Percentage by laboratory determination	potash	0·0168	0·0243	0·0369	0·0647	0·0722	0·289
	calcium	0·027	0·130	0·225	0·446	0·604	0·838
	phosphate	0·0031		0·0053	0·0107	0·0170	

The correlation coefficients* for these are: potash + 0·6807 (74 samples); calcium + 0·6501 (73 samples); phosphate + 0·6589 (72 samples), all of which are highly significant, being much above the *P* 0·01 value. Discrepancies in phosphate values are obtained with soils which are very retentive of phosphate or which lose phosphate easily. Recalculation of the correlation coefficient for phosphate, omitting the exceptional soils, gave the figure + 0·7491. The rapid tests can with advantage be used in place of laboratory analyses when many samples of soils are to be examined. E. M. P.

Lysine-content of Feeding Stuffs. C. A. Ayre. (*Biochem. J.*, 1938, **32**, 1152–1156.)—Since lysine is an essential amino-acid for normal growth, its estimation in feeding stuffs is a matter of considerable importance. Methods already in existence are either inaccurate or excessively tedious, and a method that is claimed to give accurate results has been devised. About 5 g. of protein are hydrolysed with 5 times the weight of 20 per cent. hydrochloric acid for 36 to 40 hours, and the hydrolysate is transferred to a 250-ml. Pyrex centrifuge

* The correlation coefficient is a statistical measure of the relationship between two series of observations. When observations are made it has been found that they are subject to variation and, further, constitute only a proportion or "sample" of the possible observations of the particular kind. If a number of "samples" were obtained, each would lead to its own value of a statistical constant such as the correlation coefficient and we should, therefore, obtain a distribution of values of *r* (the correlation coefficient) showing a certain amount of variation. The theoretical distribution of values of *r* has been worked out and, from it, it is possible to calculate the probability of the occurrence of a particular value. A fuller explanation of the significance of an observed correlation may be found on pages 195, *et seq*, and Table V (*a*) (page 212) of *Statistical Methods for Research Workers* (6th Edition), by R. A. Fisher.—EDITOR.

bottle. Excess of a saturated solution of phospho-24-tungstic acid is then added, and the solution is diluted with water until the final concentration of hydrochloric acid is 5 per cent. The mixture is allowed to stand overnight at room temperature, and the precipitate of phosphotungstates is centrifuged off. It is then washed twice by stirring with 25 ml. quantities of a 2·5 per cent. solution of phospho-24-tungstic acid in 5 per cent. (by weight) sulphuric acid and centrifuging. The phosphotungstates are decomposed by adding 50 ml. of water containing 1 ml. of conc. sulphuric acid and a liberal quantity of a mixture of amyl alcohol and ether, and the mixture is centrifuged. The two phases are poured into a separating funnel, and the residue, which consists of acid-insoluble humin, humin precipitated by phosphotungstic acid and ammonium phosphotungstate, is washed twice with acidified water and the amyl alcohol and ether mixture. The combined centrifugate and washings are allowed to separate and the aqueous phase is drawn off and extracted three times with the mixture of amyl alcohol and ether. The combined extracts are shaken once with a little acidified water and the aqueous solution is washed once with amyl alcohol and ether. The combined aqueous solutions are given a final washing with a little of the amyl alcohol and ether mixture. By means of this procedure the phosphotungstic acid is removed completely by the amyl alcohol and ether mixture, leaving the bases in the aqueous solution.

With samples of blood meal it was found more satisfactory to decompose the phosphotungstates with 50 ml. of acidified water and 75 ml. of the amyl alcohol and ether mixture. On centrifuging, the organic liquid forms the bottom phase and the aqueous layer can be syphoned off. The residual amyl alcohol and ether is washed three times with 25-ml. portions of acidified water and centrifuged.

The final aqueous solution is concentrated under reduced pressure and transferred to a 250-ml. Pyrex centrifuge bottle. This is heated in a boiling water-bath and excess of solid silver oxide is added in small quantities at a time with vigorous stirring. The solution is cooled and made distinctly alkaline to Nile blue or alizarin yellow S by adding warm saturated baryta solution. The precipitate is centrifuged and washed twice with small amounts of cold saturated baryta solution. The centrifugate and washings are made acid to Congo red and saturated with hydrogen sulphide under pressure. The mixture of barium sulphate and silver sulphide is centrifuged and washed. The aqueous solution is concentrated under reduced pressure and made up to 100 ml., 1-ml. portions being taken for the determination of total nitrogen. The remaining solution is treated with barium carbonate to remove sulphuric acid, and the barium sulphate is centrifuged off and washed. The centrifugate is concentrated in presence of a little barium carbonate, and the barium sulphate and excess of barium carbonate are filtered off. The filtrate is concentrated to 2 ml., and the distillation apparatus is washed down with 5 to 10 ml. of 93 per cent. alcohol. For each mg. of nitrogen present in solution, half the quantity of picric acid required to form lysine picrate is then added. The lysine picrate, which crystallises out on standing overnight at 0° C., is filtered on to a sintered glass crucible and washed with cold absolute alcohol. The filtrate is treated with a further small quantity of alcoholic picric acid solution, and the second crop of crude lysine picrate is filtered off, the same crucible as before being used. The picrate is dried, weighed and dissolved in hot water, and

the solution is concentrated and left to crystallise. The purified lysine picrate is filtered off, the filtrate is concentrated to obtain a second crop and again filtered, and the combined crops of crystals are dried and weighed. A correction of 3·4 mg. per ml. of filtrate is applied for the solubility of lysine picrate. The first crop should explode at 266°–267° C., and the second crop above 250° C. The time required for a complete analysis, in duplicate, is three days. The method was used for casein and blood meal, and gave lower results than analyses carried out by the Van Slyke procedure. It did not give satisfactory results with wheat gluten containing a low percentage of lysine, probably because of the high content of proline, which would be present in the final lysine fraction and would inhibit the crystallisation of lysine picrate. F. A. R.

Photocolorimetric Determination of Sugars in Plant Materials. W. T. Forsee, Jr. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 411–412.)—Sugars in plant materials may be determined rapidly and accurately by a modification of Hoffman's photocolorimetric method for the determination of glucose in blood and urine (*J. Biol. Chem.*, 1937, **120**, 51). The method is simple and only one standard solution—alkaline ferricyanide—is required. The standard reagent consists of 1·8000 g. of potassium ferricyanide, purified as directed by Peters and Van Slyke (*cf. Quantitative Clinical Chemistry, Methods*, 1932, p. 462), and 40 g. of anhydrous sodium carbonate in 1 litre of water. In the author's experiments a Çenco–Sheard–Sanford photoelectric colorimeter, with a blue filter and 12-ml. absorption cells, was used. To calibrate the colorimeter, 2 ml. of solutions containing from 0 to 0·4 mg. of pure glucose were placed in test-tubes or centrifuge tubes marked for 15 ml., exactly 3 ml. of the reagent were added, and the tubes were immersed in boiling water for 5 minutes, and then cooled, and their contents were made up to 15 ml. with water. The colour intensities were measured in the colorimeter set at 100 with water, a blue filter being used. The micro-ammeter readings were plotted against milligrams of glucose on semilogarithmic paper; the standard curve remained unchanged for 5 months. Plant extracts were prepared by extracting weighed samples of green or quickly-dried plants with hot 80 per cent. alcohol as usual and evaporating the alcohol on the steam-bath. Known volumes of plant juices were heated in a boiling water-bath to destroy enzymic activity, and the solutions were clarified and freed from colouring matter (*cf.* Hassid, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 138). For the clarification a sample containing from 5 to 35 mg. of reducing sugar was evaporated to about 10 ml. on the water-bath and treated with 5 ml. of a saturated solution of neutral lead acetate, and the excess of lead was removed by adding 10 ml. of a saturated solution of disodium phosphate. About 0·3 g. of Norit decolorising charcoal was added and the mixture was allowed to stand, with frequent shaking, for 30 minutes, after which it was filtered through a thin layer of talc on a Buchner funnel (*cf.* Hassid, *loc. cit.*). The original container and the funnel were washed several times with a little water, and the filtrate was transferred to a 100 or 200-ml. graduated flask. A measured volume, not more than 2 ml., containing 0·1 to 0·35 mg. of glucose, was transferred to a 15-ml. centrifuge tube, diluted to 2 ml., and treated as described above for the standard. The weight of glucose was read

directly from the calibration curve. To determine total sugars, measured volumes of 50 ml. of clarified extract were taken in 100-ml. graduated flasks and brought to the acid colour of methyl red by the addition of dilute acetic acid, the quantity of acid required being determined on a separate portion of 5 or 10 ml. After addition of 2 to 4 drops of a 1 per cent. solution of Wallerstein's invertase the solutions were kept overnight at room temperature. They were then made up to the marks and the determinations were made on measured volumes as described above. Blank determinations were also made on the invertase solution. Tables of the results of experimental work show that neither the clarification process nor the reagents influence the colour as read in the colorimeter and that slight variations in the procedure cause no appreciable differences in the results. The method gives results from 0 to 6·20 per cent. higher than those obtained by the Quisumbing–Thomas method. The method gives good recovery of glucose and sucrose added to plant materials; the sucrose was calculated from the difference between total and reducing sugars by means of the factor 0·97 (*cf. Assoc. Off. Agr. Chem., Official and Tentative Methods of Analysis*, 4th Ed., 1935, p. 135). E. B. D.

Colorimetric Determination of Rotenone. S. Schonberg. (*Ann. Falsif.*, 1938, **31**, 290–295.)—The various methods proposed for the determination of rotenone are discussed and, under given conditions, the most satisfactory one was found to be Goodhue's modification of the Gross and Smith method (*J.A.O.A.*, 1936, **19**, 118; Abst., ANALYST, 1936, **61**, 355). One g. of material is extracted for 5 or 6 hours with 100 ml. of acetone, the acetone solution is made up to 100 ml., and 2 ml. (containing 0·025 to 0·25 mg. of rotenone) are taken. To this are added 2 ml. of a mixture of 1 vol. of an alcoholic solution of sodium nitrite (1 g. $NaNO_2$ in 10 ml. of water, of which 1 ml. is diluted to 100 ml. with 95 per cent. alcohol) and 7 vol. of dilute sulphuric acid (1 vol. acid and 3 vol. water), and, after shaking, the liquid is heated for 5 minutes in a water-bath at 25° to 30° C. The dilute acid is then run down the side of the test-tube and after being heated for 15 minutes in the water-bath the tube is corked and shaken. A stable red colour results after the tube has stood for at least 2 hours, and this colour is compared with those of a series of acetone solutions of pure rotenone which have been treated in the same way as the sample. The results were found to agree with those obtained by the biological method, and the method is applicable to small quantities of rotenone and is not interfered with by pyrethrins or products of oxidation.
D. G. H.

Effect of Different Soil Colloids and Whole Soils on the Toxicity of Sodium Selenate to Millet. P. L. Gile, H. W. Lakin and H. G. Byers. (*J. Agric. Res.*, 1938, **57**, 1–20.)—The investigation was made by vegetative experiments on pot-grown millet, using quartz sand, soil and sand-soil mixtures, and the measure of toxicity used was the quantity of selenate required to reduce the yield by one half. It is concluded that about 1·5 p.p.m. or 3 lbs. per acre of selenium as selenate would be distinctly injurious to millet on most soils, although the calculation from pot to acre is not taken as reliable, even though the figures are in harmony with field observations. When the proportion of sulphate in the

soil is high, the amount of selenate required to reduce the yield by one half may be two or three times as much as when the sulphate is only adequate for maximum growth. With the same proportion of sulphate in the soils, sodium selenate is as toxic in sand-soil mixtures containing 1 per cent. of various soil colloids as in pure quartz sand, but is slightly less toxic in whole soils. This appears to be due rather to the general effect of the colloids than to any specific reaction between colloid and selenate. Such differences in toxicity bear no relation to the ratios of silica to sesquioxides in the soil colloids. Marquis wheat grown for 48 days required 1½ times as much selenate as millet grown to the jointing stage to bring about half yields. Work now in progress with sodium selenite is yielding results that differ from those obtained with the selenate. D. G. H.

Organic

Determination of Formaldehyde in Dilute Solutions and in the presence of Interfering Substances. O. Heim. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 431.)—The presence of oil of cinnamon (containing an aldehyde) in a fluid pharmaceutical preparation prevented the determination of formaldehyde by the ammonia, cyanide, hydrogen peroxide, or iodine method. The deep red colour of the preparation prevented colorimetric determination, and the small amount of formaldehyde (about 0·003 per cent.) present could not be recovered by distillation. Satisfactory results were obtained with a modification of Heim's silver method (*cf. Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 128) used with mixtures of known formaldehyde-content. Reducing sugars do not interfere with this modification. *Method.*—The aqueous or dilute alcoholic fluid is extracted four or five times with a mixture of ether and petroleum spirit (1 : 2) to remove flavouring substances, etc. The volume of solvent each time is one-half that of the fluid. To 10 ml. of the fluid after extraction, 100 ml. of a 0·1 *M* silver nitrate solution, 1 ml. of hydrochloric acid (37 per cent.), and 3 ml. of a 25 per cent. solution of sodium hydroxide are added in rapid succession, the flask being whirled once after each addition, and finally ten times. The mixture is filtered through paper and the residue is washed free from chloride. The reduced silver is then dissolved in warm dilute (1 : 3) nitric acid, the residue is washed with hot water, and the silver is titrated with *N*/10 ammonium thiocyanate solution, ferric alum being used as indicator. The time of determination is approximately 30 minutes, and the average percentage reproducibility is of the order of 2 units in the third decimal place.

By this method, the result of analysis of an aqueous 0·20 per cent. solution of formaldehyde, freshly made from about 37 per cent. stock, was 0·19 per cent. formaldehyde, both before and after extraction. A mixture of 10 ml. of the solution after extraction and 10 ml. of the treated sample gave 0·097 per cent. of formaldehyde. By the cyanide method (*Assoc. Off. Agr. Chem., Official and Tentative Methods*, 1935, p. 62), the author found only 0·009 per cent. of formaldehyde in the 0·20 per cent. solution, both before and after extraction. A little freshly made silver chloride in a slight excess of sodium hydroxide solution turns light bluish-grey in about one minute with an approximately 0·2 per cent. acetaldehyde solution; with a similar solution of formaldehyde the silver chloride turns black immediately. E. B. D.

Rapid Method for the Determination of Glycerol in Aqueous Solutions. O. Juhlin. (*Z. anal. Chem.*, 1938, **113**, 339–340.)—The acetin method for the determination of glycerol is unreliable, owing to hydrolysis, if the glycerol-content of the sample is less than 50 per cent., and the dichromate method gives high results if oxidisable impurities are present. The following rapid method is not subject to either of these drawbacks:—A quantity of the sample equivalent to 0·002 to 0·004 g. of 100 per cent. glycerol is weighed into an Erlenmeyer flask and neutralised with 0·1 *N* potassium hydroxide solution, with methyl orange as indicator, and 10 ml. of a 0·1 per cent. solution of bromine water are then added. The flask is closed with a stopper which has been moistened with a solution of potassium iodide, and after the contents have stood (without shaking) for 15 minutes, 10 ml. of a 10 per cent. solution of potassium iodide and 50 to 100 ml. of water are added, and the iodine liberated is titrated with 0·02 *N* sodium thiosulphate solution, with starch as indicator. Since the reaction-products are $(CH_2OH)_2.CO$ and hydrobromic acid, the percentage of glycerol present is given by $9206{\cdot}4\,n\,(a–b)/2e$, where *a* and *b* ml. are the titration results obtained in a blank experiment and with the sample, respectively; *n* is the strength (normality) of the thiosulphate solution, and *e* mg. is the quantity of sample taken. J. G.

Determination of Alkoxyl by the Method of Vieböck and Schwappach. S. Kinsman and C. R. Noller. (*Ind. Eng. Chem., Anal. Ed.*, 1938, **10**, 424.)—According to Vieböck and Schwappach (*Ber.*, 1930, **63**, 2818), in their modification of the Zeisel determination of methoxyl the addition of formic acid to destroy excess of bromine should give a light-coloured solution. The authors confirmed this for blank tests, but with samples the solution became darker on addition of formic acid. This was not remedied by the use of a larger quantity of acetate. Experiments showed that the bromine present originally was insufficient to oxidise all the iodine monobromide to iodic acid. All previous directions state that 6 to 7 drops of bromine should be added for a 20 to 50 mg. sample, the weight of the sample being such that a convenient amount of *N*/10 thiosulphate solution is used. The authors found that a medicine dropper with an approximately 0·7 mm. opening delivered an average of 0·023 g. of bromine per drop. With an opening of this diameter about 9 drops are theoretically necessary if 25 ml. of the thiosulphate solution are used for the titration, and about 0·3 g. (or 0·1 ml.) of bromine for 10 mg. of methoxyl or 15 mg. of ethoxyl is required to give sufficient excess of bromine. (One ml. of *N*/10 thiosulphate solution is approximately equal to 0·5 mg. of methoxyl or 0·75 mg. of ethoxyl.) Reference is made to the excellent results obtained by Clark (*J. Assoc. Off. Agr. Chem.*, 1932, **15**, 136; Abst., ANALYST, 1932, **56**, 402) and Bruckner (*Mikrochem.*, 1933, **12**, 153; Abst., ANALYST, 1933, **57**, 178) with the Vieböck and Schwappach method. E. B. D.

Gravimetric Determination of the Naphthols by Means of Formaldehyde. A. Castiglioni. (*Z. anal. Chem.*, 1938, **113**, 428–430.)—A solution of the sample in the minimum quantity of 95 per cent. alcohol is diluted to a known volume with water, and to 50 ml. of this are added 20 ml. of a 40 per cent. solution of formaldehyde and 10 ml. of conc. hydrochloric acid. The mixture is heated for 3 hours on the water-bath, and the resulting precipitate is then removed by

filtration, washed free from acid with water, dried at 100° C. and weighed. Under these conditions 2 mol. of α-naphthol are converted quantitatively into 1 mol. of dinaphthol methane, $CH_2(C_{10}H_6OH)_2$, which is white, and this then becomes oxidised to the red-brown dinaphthol carbinol $OH.CH(C_{10}H_6OH)_2$, which is the precipitate weighed (*cf.* Castiglioni, *Gazz. Chim. Ital.*, 1937, **67**, 324; Abst., ANALYST, 1937, **62**, 686). If β-naphthol is present, 2 mol. are converted quantitatively into 1 mol. of the red coloured α, β-dinaphthopyran, $CH_2(C_{10}H_6)_2O$, m.p. 185° C., which may be regarded as being formed by the elimination of a molecule of water from the hydroxyl groups of dinaphthol methane (*cf.* K. Dziewonski and St. Pizon, *Chem. Zentr.*, 1934, **105**, (1), 3593). The colour of the precipitate is an indication of whether α- or β-naphthol is present, but if there is any doubt a portion of the weighed precipitate should be dissolved in a conc. solution of sodium hydroxide; a blue colour then indicates the presence of α-naphthol. The method is unsuitable for mixtures of the naphthols, but if the blue colour is produced by heating the original sample with the alkali and formaldehyde (*cf.* J. Breslauer and A. Pictet, *Ber.*, 1907, **40**, 3786) it may be used for the rapid colorimetric determination of α-naphthol. Determinations made on 0·07 to 0·6 g. of either naphthol gave results showing a maximum error of −0·1 to ±0·3 mg. J. G.

Thiocyanogen Value of Sardine and Herring Oils. S. Ueno. (*J. Soc. Chem. Ind., Japan*, 1938, **41**, 200B.)—Even with samples of the same kind of fish oil, the thiocyanogen and iodine values are not always parallel. Analyses of sardine and herring oils gave the following results:

Oil	Experiment	Oil produced in	Iodine value	Thiocyanogen value
Herring	1	Hokkaido	102·0	69·5
,,	2	Karafuto	101·2	68·8
,,	3	,,	116·7	73·5
,,	4	Hokkaido	101·0	70·8
,,	5	—	104·3	72·9
,,	6	—	99·7	70·1
Sardine	7	Honshu	179·8	90·2
,,	8	Hokkaido	178·1	86·1
,,	9	Chosen	181·6	91·0
,,	10	,,	180·3	84·2
,,	11	,,	182·6	89·5
,,	12	,,	175·2	89·7
,,	13	,,	179·1	89·9
,,	14	Hokkaido	171·6	90·2
,,	15	,,	183·5	90·7
,,	16	,,	184·1	89·9
,,	17	,,	184·3	88·2
,,	18	,,	179·6	91·4
,,	19	Honshu	180·1	89·1

Results of analyses of mixtures of these two oils are also given, and the saponification values, acid values and colour of all the oils examined are included in the original tables. No explanation of the lack of parallelism is offered. E. B. D.

Relation between Thiocyanogen Value and Iodine Value during Oil-hardening. S. Ueno. (*J. Soc. Chem. Ind., Japan*, 1938, **41**, 200B–202B.)—Sardine oil was hardened experimentally under the same conditions as in large-scale commercial work. Nickel on kieselguhr was used as the catalyst, the ratio of nickel to oil being 1 : 200. The iodine and thiocyanogen values were determined on samples of the oil taken hourly during hydrogenation; melting points were determined also on these samples. Two samples of oil were hydrogenated at pressures of 5 to 7 atmos. and two at atmospheric pressure, at about 180° C. The results are tabulated and curves showing the rate of decrease in iodine value and thiocyanogen value are given. The curves show a rapid decrease in thiocyanogen values at the times when the iodine values are between 70 and 80. It is considered that this indicates the selective and stepwise character of the hydrogenation.

E. B. D.

Norwegian Draft Standards. Rules for the Sampling and Testing of Whale Oil. (*Norsk Hvalfangst-Tidende* (*The Norwegian Whaling Gazette*), **1938**, **27**, [4], 111–138.)—See ANALYST, 1938, 652.

Determination of Alkali in Wool. S. R. Trotman and D. E. Stocker. (*J. Text. Inst.*, 1938, **29**, 148.)—If wool containing alkali and soap is treated with an alcoholic solution of oleic acid, free alkali is converted into soap, and soap is unaffected. By using a standard solution of oleic acid the alkali can be determined by titration. A weighed quantity (1 to 2 g.) of the wool is heated on the water-bath with a known volume of the oleic acid solution until the alcohol has evaporated and the carbon dioxide has been expelled. The wool is then transferred to an extractor (the beaker being washed out with several small quantities of alcohol) and extracted for about an hour with boiling alcohol, after which the extract is boiled (to ensure absence of carbon dioxide) and titrated with $N/10$ alcoholic potassium hydroxide, with phenolphthalein as indicator. The oleic acid solution is also titrated and the alkali is obtained by difference. Test determinations in which 2 ml. of $N/10$ sodium carbonate solution were added to 1 g. of purified wool gave results ranging from 2·01 to 2·10 ml. of $N/10$ alkali. A sample of Botany top (alkaline to phenolphthalein) gave 0·31 to 0·33 per cent. of alkali.

Measurement of the Oxygen Absorbed by Vulcanised Rubber in Air. A. G. Milligan and J. E. Shaw. (*Reprint; Paper at Rubber Technology Conference, London*, 1938, May 23–25th.)—It is proposed to measure the ageing quality of rubber directly by the rate of oxidation. The apparatus consists of a number of graduated glass tubes containing mercury and closed at the top with ground-glass stoppers with mercury seals. The bottom of each tube is connected with an open tube and any pair of tubes can be connected by a tap with a common reservoir of mercury, the level of which is adjustable. The tubes are attached to the inside of the door of a glass-fronted air thermostat, the taps and reservoir being outside. A sample of rubber, rasped to a coarse powder, is weighed into an iron gauze basket. It is hung overnight in the oven at the temperature of the test, then suspended with a phosphorus pentoxide tube, from the stopper of the graduated

tube, which is then sealed, and the oven is closed. After the required temperature is regained the pressure in the closed tube is adjusted to that of the atmosphere, and the volume of air is noted and corrected to N.T.P. Readings may be taken morning and evening; half a dozen results should be ample to determine the slope of the oxygen absorption/time curve. At a given temperature the ageing quality of rubber can be estimated much more rapidly than by following the decay of tensile strength. Also, in a given time determinations can be made at a lower temperature, and temperatures need not be far from service temperatures. The correlation between the two methods is good and the authors consider the oxygen absorption method affords a more fundamental index of decay than measurement of physical properties. The new method requires only a single sample, which can be obtained from any rubber article by rasping, for the whole test. For fuller experimental details the original paper should be consulted. E. B. D.

Methods for Evaluating Carbon Blacks. I. Drogin. (*Reprint, Rubber Technology Conference, London,* May 23–25th, 1938.)—Satisfactory correlation was not obtained between the results obtained by the original methods of testing the channel-process carbon blacks used in rubber and the actual behaviour of the blacks in processing and reinforcement. These tests were based on the physical and chemical properties of the blacks. Further tests, which were then devised for the study of the vulcanised and unvulcanised carbon black-rubber compound, were also unsatisfactory. Recently, the sensitivity of existing laboratory tests has been increased and several new tests have been developed. These include:—(1) The St. Joe compression flexometer test, for measuring the rate of heat generation and the resistance to breakdown of a rubber compound subjected to repeated distortions under compression; (2) the impact test, for measuring the linear indentation and rebound after repeated impacts under pendulum action; (3) the T-50 test, which gives information on the state of vulcanisation by determining the temperature at which a previously stretched and frozen sample of rubber compound will contract to half the stretched elongation when gradually warmed; (4) the test of dielectric properties. Compounds which give similar results by the former strain and stress tests often show pronounced differences with these newer tests. This point is illustrated by numerous comparative results. Tables are given showing the influence of the various physical and chemical characteristics of the blacks on the properties of the rubber compounds; the limits of values observed for each characteristic are stated. Further research, especially on differences in particle size distribution, nature of volatile matter, surface chemistry, and wetting characteristics is required. The paper quotes many numerical results, and there are 52 references. E. B. D.

Inorganic

Analysis of Chromium Nitride. H. Ter Meulen. (*Rec. Trav. Chim. Pays-Bas,* 1938, **57**, 591–593.)—The chromium determination is done by the usual method, *e.g.* fusion with sodium carbonate and potassium nitrate. The only direct method by which the author succeeded in determining the nitrogen is the following:—The nitride (0·1 g.) is mixed with sodium peroxide (1 g.) in a platinum

boat, which is placed in a quartz tube. The air is displaced by a current of pure oxygen, and the tube is cautiously heated. A vigorous reaction sets in, the nitrogen being liberated. The gas is collected over alkaline pyrogallol solution, and the pure nitrogen measured. The oxygen used must be tested for nitrogen, and if any is found, a measured volume of oxygen should be used in the analysis and a suitable correction applied. W. R. S.

Accurate Determination of Magnesia and Lime in Technical Sodium Chloride. C. Tanne. (*Chem. Ztg.*, 1938, **62**, 572–573.)—The usual amount of salt taken for the determination of magnesia and lime is 10 g. When three (ten) times the amount of salt was taken, both the magnesia and lime results fell to one-third (one-tenth) the figure found in 10 g. Proportional increases in the lime and magnesia contents were found when 6·6 and 3·3 g. of salt were taken. Synthetic tests proved that this anomaly does not occur when chemically pure sodium chloride is substituted for the technical product obtained by evaporation *in vacuo*; yet after vacuum evaporation of a solution of the chemically pure salt with a known small amount of magnesium sulphate, the magnesia recovery is inversely proportional to the quantity of salt used for the determination. The author appeals to his confrères for the correct interpretation of the observed facts and for a reliable method for the determination of lime and magnesia in sodium chloride. W. R. S.

Analysis of Phosphate Rock. J. I. Hoffman and G. E. F. Lundell. (*Research Paper* RP1095, *National Bureau of Standards, U.S.A. Dept. of Commerce*, May, 1938.)—The methods used at the National Bureau of Standards in the analysis of the two Standard Samples of Phosphate Rock, 56*a* and 120, are described, and a summary of the results obtained by nine co-operating analysts is given. Most of the methods that were used when the first Standard Sample of Phosphate Rock was issued (*J. Assoc. Off. Agric. Chem.*, 1924, **8**, 184) are still in use, but modifications of many of them have been adopted, and the present paper brings the previous methods up to date. Spectrochemical analyses of the two samples were made, the arc spectra being photographed in the region 247 to 330$m\mu$, with the use of carbon electrodes, and in the region 320 to 460$m\mu$, with the use of copper electrodes. The elements found were:—Calcium, aluminium, iron, magnesium and silicon as major constituents; manganese, sodium, potassium, chromium, strontium, copper, titanium, nickel and vanadium as minor constituents; lead, tin, boron and nickel in traces. The boron was quantitatively determined, a sample of tricalcium phosphate practically free from boron being used as a base. The sensitivity of the test for boron is approximately 0·0001 per cent. The amounts (as B_2O_3) found were:—in 56*a*, 0·005 per cent.; in 120, less than 0·001 per cent.

Analysis of Harrogate Fango (Therapeutic Mud). A. Woodmansey. (*Harrogate Spa J.*, 1938, **1**, 29.)—This is a natural colloidal medium occurring in an irregular bed which has been deposited over the oldest exposed geological stratum in the district, a shale member of the Lower Carboniferous system, found at Harlow within the borough boundary. The material is mixed with the mineral water to the consistence required for application. A sample contained:—Water,

34·3; solid matter, 65·7 per cent. The constituents calculated on the dry substance were:—Organic matter, 11·57; water-soluble substances, 1·59; acid-soluble substances, 13·78; insoluble matter, 72·6 per cent. The water-soluble matter contained siliceous matter, iron, calcium (0·49 per cent.), magnesium, sodium (0·30 per cent.), potassium, lithium, chloride (0·46 per cent.), sulphate and sulphide. The acid-soluble matter contained 5·42 per cent. of silicate, 5·42 per cent. of iron (ferrous and ferric), 2·02 per cent. of aluminium, calcium, magnesium, traces of copper and manganese and 3·0 per cent. of carbonate (CO_3). The insoluble matter consisted of: silica, 54·5; iron oxide, 1·0; alumina, 13·1; manganese oxide, 0·1; calcium oxide, 0·2; magnesium oxide, 3·7 per cent.; titanium, a trace.

Quinic Acid as a Fluorescence Indicator. L. Szebellédy and J. Jónás. (*Z. anal. Chem.*, 1938, **113**, 266–275.)—Quinic acid (6-methoxy-γ-quinoline-carboxylic acid) in acid solution fluoresces bright yellow in ultra-violet light, whilst in alkaline solution it fluoresces blue. One γ of the acid still gives a noticeable fluorescence in 5 ml. of *N* nitric acid. The same degree of visibility obtains in alkaline solution; the transition point is situated between *p*H 4·0 and 5·0. The common anions and cations have little influence on the fluorescence of quinic acid, which can be used with advantage for the titration of strongly-coloured solutions. W. R. S.

6,7-Dimethoxy-*iso*quinoline-1-carboxylic Acid as a Fluorescence Indicator. L. Szebellédy and J. Jónás. (*Z. anal. Chem.*, 1938, **113**, 326–334.)—This indicator is best prepared by oxidation of papaverine according to the method used by G. Goldschmiedt (*Monatsh.*, 1887, **8**, 510) in his investigations into the constitution of this alkaloid; it was also obtained by Carr and Pyman (*J. Chem. Soc.*, 1914, **105**, 1591) by the oxidation of emetine and cephaeline. To a solution of 25 g. of papaverine in 2 litres of water are added slowly 5 litres of a 2 per cent. solution of potassium permanganate, and the mixture is allowed to stand at 50° C. until decolorisation is complete (about 1 day), when it is filtered. Sulphur dioxide is passed through a suspension of the residue in cold water until all manganese dioxide has dissolved, and the residual pale yellow powder is extracted with hot dilute hydrochloric acid (which removes papaveraldine in the form of the yellow needles of its hydrochloride), and then crystallised from ethyl acetate. In this way the indicator is obtained as colourless needles, m.p. 196° C.; yield 20 per cent. It is sparingly soluble in water, slightly soluble in 0·01 per cent. alcohol, and very soluble in the common organic solvents, which, however, are either immiscible with water (*e.g.* benzene or toluene), or inhibit the action of the compound as an indicator. It is therefore best to use a mixture of equal volumes of absolute alcohol and a 0·10 per cent. solution of the indicator in anhydrous glycerol, and when the solution to be titrated is colourless to add 0·2 ml. of this for every 100 ml. present. Solutions of the indicator show a yellow and blue fluorescence in filtered ultra-violet light when acid or alkaline, respectively, the range of the colour change being between *p*H 9·5 and 11·0, whatever the quantity of indicator used. The fluorescent nature of the indicator is attributed to the fluorophoric pyridine grouping attached directly to the benzene nucleus, and in this respect it is analogous to quininic acid (6-dimethyoxy-*iso*quinoline-γ-carboxylic acid); the methoxyl

group is believed to be responsible for intensification of the colour, while the salt-forming nature of the carboxyl group accounts for the change in fluorescence at different *p*H values. The limiting value of the visibility of the fluorescence of the indicator is 5, 6, 10 and 10γ in 5 ml. of *N* acetic, nitric, sulphuric or hydrochloric acid, respectively, and 6γ in 5 ml. of *N* sodium hydroxide solution. Similar values are given for various strengths of acetic acid and sodium hydroxide solution containing one of a large number of common inorganic anions and cations, amphoteric hydroxides and ammine-forming cations (*cf. Z. anal. Chem.*, 1938, **113**, 266); for such solutions the limiting value for the visibility of the fluorescence was usually between 5 and 30γ. Exceptions were the ferric, iodide, thiocyanate, copper-ammine, cobalt-ammine and nickel-ammine ions, for which the values were 50, 40, 100, 50, 300, and 50γ, respectively. The agreement of the titrations with those obtained with phenolphthalein as indicator was satisfactory, and the maximum error of titrations made in the presence of up to 30, 10 and 10 mg. of Columbia brown-R, tartrazine-XX and methylene blue in 10 ml. of 0·1 *N* sodium hydroxide solution were +0·06, +0·08 and +0·08 ml. of 0·6 *N* acetic acid, respectively. With such coloured solutions 1 ml. of indicator per 100 ml. of solution should be used. J. G.

Orcinaurine as a Fluorescence Indicator. J. Jónás and L. Szebellédy. (*Z. anal. Chem.*, 1938, **113**, 422–428.)—Orcinaurine (or homofluorescein) may be produced by the action of chloroform and sodium hydroxide (*cf.* H. Schwarz, *Ber.*, 1880, **13**, 543) or of formic acid and zinc chloride (*cf.* E. Grimaux, *Bull. Soc. Chim.*, 1891, **5**, [3], 465) on orcinol. The former reaction may be used as a test for orcinol (*e.g.* in biological specimens), for which purpose 1 ml. of an extract of the sample is warmed for 30 seconds with 1 drop of chloroform and 1 g. of sodium hydroxide; a red colour and a green fluorescence (green-yellow in ultra-violet light), which decreases in intensity on acidification, indicates the formation of orcinaurine. The fluorescence is not readily visible in visible light (*i.e.* in daylight or lamp-light) at *p*H values below 6·5, but it is developed between *p*H 6·5 and 8·0 and gives a sharp end-point. The limit of visibility in visible light is 0·4γ (1:1,250,000) in alkaline solutions, and 0·06 ml. of a 0·03 per cent. solution in water should be used for every 100 ml. of colourless solution to be titrated (3·0 ml. for coloured solutions). The lower limit of visibility in ultra-violet light of the indicator in acid solutions was found to be 2 to 10γ in the presence of 9 common anions and 24 cations, but if ferric ions were present it rose to 4,000γ; it was 1γ in *N* sulphuric, acetic or nitric acid, and 10γ in *N* hydrochloric acid. Corresponding values for alkaline solutions including those containing the common amphoteric metal hydroxides and ammine-forming cations, ranged from 0·02 to 0·4γ, and these were exceeded only in the presence of the copper-, cobalt- and nickel-ammines, when they reached 20, 10 and 1γ, respectively. Titrations of 20 ml. of 0·1 *N* sulphuric acid with 0·1 *N* sodium hydroxide solution were in agreement with those obtained with methyl red as indicator to within 0·03 ml., and with similar solutions containing up to 2 mg. of methylene blue, 40 mg. of Columbia brown R, and 20 mg. of tartrazine XX, the maximum differences between the titrations obtained for the colourless and coloured solutions were ±0·03 ml. J. G.

Microchemical

Apparatus for Drying Small Amounts of Material. F. Fuhrmann. (*Mikrochem.*, 1937–38, **23**, 167–173.)—Metal blocks of three different shapes are described. The weight of metal in the block is large compared with the weight of the apparatus to be dried, and a micro-burner with screw adjustment is used for heating, so that the temperature can be regulated to within 1° to 2° C. For convenience the three blocks and burners may be fixed on a single stand, the heat of each block being adjustable. The first type is 6 to 7 cm. in diameter and 18 mm. high. The slightly concave top surface is polished and platinised. This type is especially suited for drying material in squat dishes. The second type consists of a hollow cylinder with a thick base and thick walls, the internal dimensions being diameter 5 cm. and depth 2 cm. The inside surface is polished and platinised. A substantial lid fitted outside the cylinder is also polished and platinised on the inner surface. Two holes are bored in the lid, so that, if necessary, nitrogen or other indifferent gas or a hot or cold stream of air may be passed through during the drying. Further, by stoppering one of the holes and applying suction to the other, drying may be carried out *in vacuo*. The third type consists of a brass cylinder, about 6 cm. in diameter, containing one axial hole, 15 mm. in diameter and 40 mm. deep, and round this there are 8 holes, 10 mm. in diameter and 40 mm. deep. This apparatus is designed for the evaporation of solutions and drying of precipitates in small beakers and centrifuge tubes, and is also convenient for accelerating the solution of small precipitates, the temperature of the block then being maintained at 100° C. This block is especially useful in preparative work. The temperatures are measured by means of thermometers fitted into holes in the thickest part of the blocks. J. W. M.

Microchemical References. 1938, Part I, pp. 128. (*Supplement to Mikrochem.*, 1938, **24**).—Microchemical references, pure and applied, arranged alphabetically in order of subjects. J. W. M.

Emich Filter Sticks Applied to Work on the Gamma Scale. G. Gorbach and M. Kostic. (*Mikrochem.*, 1937–38, **23**, 176–190.)—For work on a very small scale the Kuhlmann type of balance is not sufficiently sensitive; the best balance is the Donau torsion balance on the Nernst principle (*Mikrochem.*, 1931, **9**, 1; 1933, **13**, 155), for the maximum load is 2 g, and the time required for weighing only 15 seconds. With the utmost care an accuracy in weighing of $\pm 0{\cdot}2\gamma$ may be attained. The scale is illuminated by a 40-watt lamp about 2 metres above the balance, which is protected from the direct rays by a thick piece of tinfoil. When an object is to be weighed it is placed on the balance-pan, tared, and left for exactly 3 minutes before reading. Small micro-beakers weighing 0·180 to 0·160 g., with height 15 mm., diameter 7 mm., capacity 0·5 ml., and wall thickness 0·2 to 0·3 mm., are used, for determinations on samples of 0·1 mg. or less. The filter-sticks are of the original Emich type—glass with an asbestos filtering pad—but are only 2 cm. in length, the stem being a capillary tube, 1·2 mm. in outer and 0·8 mm. in inner diameter. The filter-flask is correspondingly small. Before use the beaker and filter-stick are thoroughly cleaned by soaking in hot

chromic acid mixture, the beaker is washed with distilled water and dried at 105° C. and the filter-stick is attached to the suction flask, and water and absolute alcohol, followed by ether or acetone, are sucked through. The beaker and filter-stick are then placed in a vacuum desiccator for 45 minutes before weighing. The time between the removal from the desiccator and the final reading of the balance must always be the same. The tare is a similar beaker weighted with small pieces of platinum wire. Phosphorus in lipoids is determined on about 0·1 mg. of material. When only 1 to 5γ of phosphorus is present the strychnine molybdate method is used, but for 10 to 50γ the ammonium molybdate method is preferred. Ergosterol is determined by the method of Windaus (*Z. physiol. Chem.*, 1910, **65**, 110). The maximum error on the phosphorus determinations by the molybdate method was about −0·3 per cent. difference between the calculated and found values. By the strychnine molybdate reaction errors of 0·0 to 4·5 per cent. were obtained. The methods are applied to determinations in biological material. J. W. M.

Differentiation of Brucine and Strychnine. A. Martini. (*Mikrochem.*, 1937–38, **23**, 164–167.)—A micro-drop (0·01 ml.) of a 1 per cent. solution of brucine hydrochloride and a micro-drop of a 1 per cent. solution of strychnine acetate are placed, each on a microscope slide. On adding to each a drop of rhodium chloride solution crystalline precipitates are formed, but the crystal forms differ widely. The sensitivity of the test is about 1 to 10γ. When the two alkaloids are present together they may both be recognised when the amounts of each present are similar (1:1 or 1:2); otherwise the picrolonic acid reaction is preferable. Two photomicrographs are given. J. W. M.

Detection of Oxalic Acid in Leather. K. Klanfer and A. Luft. (*J. Inter. Soc. Leather Trades' Chem.*, 1938, **22**, 297–299.)—The micro-method of Feigl and Frehden (ANALYST, 1937, **62**, 331) has been modified for use with leather, since oxalic acid is used in the bleaching of vegetable-tanned leathers. About 0·02 g. of diphenylamine is pressed down with a glass rod on to the surface of the sample, and then heated from above with a small flame. After the diphenylamine has been in the fused state for about 1 minute 2 to 3 drops of alcohol are added, and the sample is exposed to bright daylight, when the development of a blue colour (aniline blue) indicates the presence of oxalic acid. This takes 1 to 10 hours according to the amount of oxalic acid present, and is accelerated by the action of light; the minimum quantity of the acid detectable is 5γ. The principal advantage of the method is the elimination of the preparation of an extract of the leather in water, since this contains tannins, chromium compounds and sulphates, which must be removed as they interfere with the usual calcium oxalate method. J. G.

Mercurimetric Micro-determination of Silver. J. Trtílek. (*Mikrochem.*, 1937–38, **23**, 190–194.)—The reaction of diphenylcarbazide and diphenylcarbazone with mercury renders it possible to use mercury as an indicator not only in the determination of halides, but also of silver. The factor of the 0·01 *N* mercurous nitrate is determined with pure sodium chloride and also with pure

silver in order to control the drop error of the indicator both by direct and indirect titration, the mean of 5 results being taken in each titration. In making a determination 4 ml. of silver solution (containing approximately 1 mg. of silver per ml.) are acidified with 1 ml. of 0·2 *N* nitric acid, a measured amount of sodium chloride (excess) is added, and then a few drops of the cold saturated alcoholic solution of the diphenylcarbazone indicator. The excess of chloride is titrated with 0·01 *N* mercurous nitrate until a violet colour appears. The method is particularly applicable to the determination of silver in alloys. An example is given of the analysis of an alloy of copper and silver; on a 19 mg. sample 30·30 per cent. of silver was found (mean of 3 titrations). Gravimetric control analyses gave results varying from 30·32 to 30·50 per cent. of silver. J. W. M.

Physical Methods, Apparatus, etc.

Fluorescence Analysis in Ultra-violet Light as Applied to Dyestuffs and Fibrous Materials. J. Grant. (*J. Soc. Dyers and Col.*, 1938, **54**, 361–366.) —Recent advances in the technique of the method and in the apparatus for producing ultra-violet light for fluorescence analysis are dealt with. The latter include the new type of ultra-violet lamps in which the arc is started by a switch instead of by tipping, lamps which produce concentrated beams of ultra-violet light for "close-up" examination, photographic methods, and apparatus for fluorescence microscopy in transmitted or incident light. Applications dealt with include the identification of dyestuffs and fibres, and ultra-chromatographic adsorption, in which a solution of a mixture of (*e.g.*) dyestuffs is allowed to pass down a column of a suitable adsorbing agent (*e.g.* activated alumina), the differential adsorption that occurs being observed in ultra-violet light instead of in visible light as in chromatographic analysis. An example of this nature is the use of fuller's earth to adsorb colouring matters in foodstuffs from a solution in methyl alcohol, the dyestuff being removed again subsequently from the adsorbing material by elution with a mixture of methyl alcohol, pyridine and water. Dyestuffs as closely related as Direct Sky Blue and Direct Blue 2B may be dealt with in this way (*cf.* Cook, *Chem. & Ind.*, 1936, **55**, 724). Titration (*e.g.* of chlorides in dyestuffs; see Grant, ANALYST, 1937, **62**, 285) with the aid of fluorescent adsorption and other indicators, the identification of blemishes on textiles and dyeing effects, and the fading of dyestuffs (see Grant, *id.*, 1934, **59**, 439) are also discussed. J. G.

Copper Thermostat containing Phosphoric Acid for Measurements of Kinetics (at High Temperatures). H. C. S. Snethlage. (*Chem. Weekblad*, 1938, **35**, 364.)—The author's experiences with the mixture of *o*- and *m*-phosphoric acids recommended for a bath-liquid for thermostats by Christensen and King (ANALYST, 1936, **61**, 506) are described. The thermostat used was cylindrical in shape, as for the purpose in hand this necessitated the minimum quantity of the relatively expensive phosphoric acid. It was constructed of copper plate, 4 mm. thick, external electric heating elements in an iron casing being used to maintain the temperature at 20° to 30° C. below the required value, while an internal element carried in a glass tube and actuated by a relay, served to control the

temperature more closely, *i.e.* to within 0·1° C. of the desired value. A double centrifugal stirrer was fitted, and initial heating periods of 1 and 1·5 hours were required to raise the temperature to 100° and 150° C., respectively. There was evidence of attack of the copper, especially above 160° C., and this increased in degree with the water-content of the phosphoric acid, and produced a grey-violet coating which crystallised on cooling and came apart. Attack on the base was greater than on the walls, and was considerable after 500 hours at 140° to 150° C., the base of the thermostat being then 1 mm. thinner. The attack may be minimised by protecting the base from the rapidly-moving liquid by means of a copper ring, 2 cm. high, on which is supported a loose, circular copper plate. Glass vessels immersed in the thermostat were also attacked, the loss in weight being 0·02 mg. per sq. cm. per hour at 160° C., and considerably greater at 340° C.

J. G.

Multiple Softening Point Apparatus for Bitumen. D. M. Wilson. (*Chem. & Ind.*, 1938, **57**, 767.)—Disadvantages of the standard I.P.T. apparatus for determining the softening point of bituminous materials (*Standard Methods of Testing Petroleum and its Products*) are that only one sample can be tested in duplicate at a time, and that it is difficult to ensure uniform temperature conditions in the beaker when testing materials of high m.p. The multiple apparatus now described (Fig. 1) enables 4 duplicate determinations to be made simultaneously, and provides for mechanical stirring at 75 r.p.m. and for increasing the temperature at the standard rate by an electrical method. The beaker (capacity 1500 ml.) is lagged with asbestos and has 2 observation windows, and the electric heater on which it stands is controlled by a rheostat which is adjusted by hand as required so as to maintain the rate of increase of temperature within the prescribed limits. A small retaining plate serves to locate each of the 8 balls in the centre of its respective ring, and it may be lowered when these are in position. Any difficulty in transferring the apparatus to the bath is thus avoided, as the balls pass freely through the guide-plate when the softening-point is reached. The rings are filled with the samples in the standard way, and the observation of the softening point is facilitated by means of a small electric light in the beaker. When results are required very rapidly, a sufficient degree of accuracy is obtained by filling the rings with the sample, the excess of which is cut off when the bitumens have cooled.

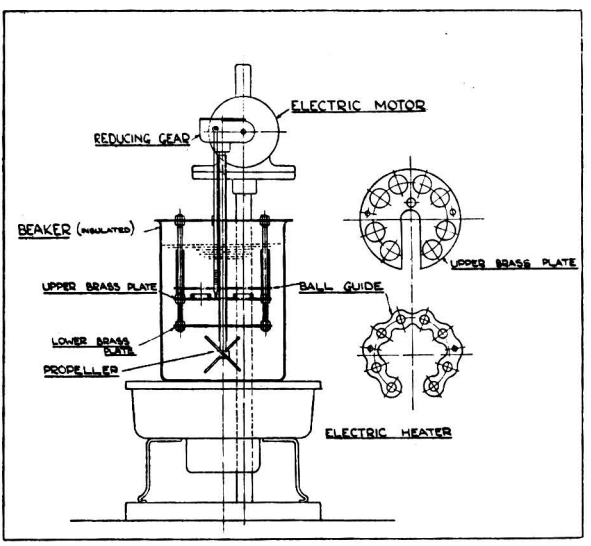

FIG. 1

The filled rings are immersed in water at 0° C. for 10 minutes, and are then at once transferred to the apparatus and the test is carried out. This procedure also avoids a difficulty experienced with certain soft bitumens when tested by the standard method, as with such samples the balls sink into the bitumen and cause it to bulge below the ring. Comparative tests on 4 specimens having softening points of 37·5° to 92·5° C. (Standard I.P.T. method) showed good agreement between the results obtained by the standard apparatus and the multiple apparatus whether the standard or rapid procedure was employed; the maximum divergence from the standard value was 1·5° C. J. G.

Simple Method for the Determination of the Birefringence of Fibres. R. H. Marriott. (*J. Inter. Soc. Leather Trades' Chem.*, 1938, **22**, 294–297.)—It has been shown (*cf.* Marriott, *id.*, 1935, **19**, 246) that the method used for the determination of the double refraction of crystals in petrology (*i.e.* from measurements of the thickness of quartz necessary to equalise the paths of the ordinary and extraordinary rays, which enables the retardation of one ray relative to the other to be obtained) may be applied to fibres of leather, silk and hair. Disadvantages arising from the expense of the quartz wedge, the fact that each fibre must be placed accurately on the cross-wires, and difficulties of technique have now been eliminated by replacing the wedge by a thin plate of mica. If this is inserted between crossed nicols, then on rotating the polariser increasing amounts of retardation between the two transmitted rays may be obtained, and if the plate has a suitable thickness, a position of the polariser will be found for which a doubly-refracting fibre placed between the analyser and the mica plate appears black on a luminous background; the extent of rotation of the nicol necessary for this depends on, and therefore is a measure of, the magnitude of the double refraction of the fibre. The optimum thickness of the mica plate is that which produces a difference of one quarter of a wave-length of light in the phase of the two emergent beams of light. Such plates are known as "quarter wave plates," and are obtainable from most opticians, or they may be made by splitting off thin layers of mica with a fine needle until one having the above-mentioned properties is obtained; a sorting test is the blue-grey and yellow colour transmitted at the position of maximum brightness and when the nicols are parallel, respectively, daylight being the illuminant. Where very accurate results are required the plate should be selected by the method of convergent polarised light (see Johannsen, *Manual of Petrographic Methods*); or, by calculating, by proportion, the actual retardation due to the plate selected from the amount of rotation of the polariser necessary to reduce the brightness of the field from a maximum to a minimum value in monochromatic light. For less accurate work the mica may be replaced by a piece of ordinary cellophane ("300" thickness) which has a retardation of about $\frac{1}{3}$ wave-length. A fibre placed at 45° to the planes of the nicols, therefore, becomes non-luminous when the retardation is equal and opposite to that produced by rotating the polariser. For leather the nicols are crossed, and the mica or other plate is inserted under the stage of the microscope (on which is placed a section of the sample), and above the polariser. Then unless the fibres are isotropic, rotation of the sample will ensure that some of them make an angle of 45° with the plane of vibration, so that

a certain degree of luminosity will be observed. The angular rotation of the polariser necessary to produce the maximum degree of darkness is then measured, each degree of rotation being equivalent to a retardation given by the wave-length of the light used divided by the angular rotation equivalent to a retardation of one wave-length (*i.e.* 180°). With the sodium D-line (wave-length 589$m\mu$) this is 3·27$m\mu$ per degree. The rotation is independent of the wave-length, the retardation being a linear function of the rotation of the polariser, so that calibration for each wave-length of light (as in the wedge method) is avoided. The type of anisotropy shown by a fibre, *i.e.* whether the elongation is positive or negative, may also be determined, because with a positive elongation the ray vibrating in the direction of the long axis of the fibre is transmitted more slowly than the ray vibrating at a right-angle to it, and *vice-versa*. Since all chrome leathers and raw fibres have a positive elongation, a sample of this nature may be used in a preliminary experiment in order to determine which is the "slow" direction of the mica plate. This plane of vibration should then be arranged so that it is parallel to that of the analyser, and the fibres from the sample are oriented in the south-west to north-east direction (as seen under the microscope); then if compensation is obtained by rotating the polariser in a clockwise direction the fibres possess positive elongation, and *vice-versa*. The angular rotation of the polariser may be measured by means of a pointer attached to the polariser, and a protractor having a hole through which the polariser passes. J. G.

Reviews

BRITISH CHEMICAL INDUSTRY: ITS RISE AND DEVELOPMENT. By Sir GILBERT D. MORGAN and DAVID DOIG PRATT. Pp. xii + 387. London: Edward Arnold & Co. 1938. Price 21s.

Sir Gilbert Morgan and Dr. Pratt, as might have been expected, have given us a genuine contribution to technical literature. Not only have they drawn upon their own encyclopaedic knowledge, but they have been singularly successful in securing the co-operation of some of the most eminent men in our profession. In fact, in scanning the list of acknowledgments, one feels that the production has, indeed, an all-star cast.

We are grateful to the authors that they have helped to explode the vulgar belief that the British Chemical Industry is a post-war development. Certainly the industry has become less painfully shy and inarticulate than of yore, but even before the war there were few branches of our industry which did not compare favourably in results with any of our competitors, and our failures were usually occasioned more by the overriding political interests of the country, than by any lack of enterprise on the part of our manufacturers.

All through this book a fine sense of proportion has been maintained, and here indeed is a valuable guide to all anxious to traverse the wide domain of chemical industry. A mere list of the contents is illuminating and cannot be omitted—Salt; Sulphur; Sand, Clay and Limestone; Industrial Gases; Selected Metallurgical Processes; Borax and Phosphate; Paints and Pigments; Oils, Fats

and Waxes; Cellulose; Coal; Oil, Shale and Petroleum; Explosives; Dyestuffs and Intermediates; Plastics and Rubber; Industrial Solvents; Fine Chemicals—all have adequate place. Each subject is clearly dealt with, and the maximum amount of detail which a work of this size permits is provided.

It must, of course, be borne in mind that, owing to the vast area covered, this book is more in the nature of a touring map, and not a collection of detailed large-scale surveys of each individual district, in which we can expect to find clearly marked the tiny hamlets and delightful nooks which are so dear to those intimately familiar with the particular spots.

In these days the chemical plant manufacturers issue such magnificent catalogues, replete with photographic reproductions of plant, that it must be a sad temptation to some authors to make free use of this material, and this makes us all the more grateful to the authors for their wise discrimination.

This book is specially welcome nowadays, when so many of us have, perforce, our actual experience confined within fairly narrow limits, and it cannot fail to be of interest and value to all those who aspire to be chemically-minded.

W. A. S. CALDER

INORGANIC COLLOID CHEMISTRY. By H. B. WEISER. Vol. III. THE COLLOIDAL SALTS. Pp. viii + 473. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 30s.

The two previous volumes of this series of three were reviewed in THE ANALYST (1933, **58**, 787, and 1936, **61**, 69), and merited high praise. This final volume completes a remarkable study of Colloid Chemistry as exhibited in the field of inorganic materials, elements and compounds.

The colloidal salts offer a wide field for investigation into both academic problems and technology. As the Preface informs us, special consideration has been given to: the velocity of precipitation and the physical character of precipitates; the stability of sols and the mechanism of the electrolyte coagulation process; ion antagonism in colloid systems; the mutual coagulation process; adsorption on ion lattices; adsorption indicators; the colour of colloids; the permeability of membranes; the phenomena of thixotropy and rheopexy. On the technical side there are discussed: plaster of Paris; lithopone and other sulphide pigments; Prussian blue; the colloidal halides in photography; the base-exchange phenomenon in silicate gels; the inorganic colloids of the soil; Portland and aluminous cements.

The book is divided into five parts: the colloidal sulphates and related compounds; the colloidal halides; the colloidal sulphides; the colloidal ferrocyanides and ferricyanides; the colloidal silicates. There are twenty-three chapters and adequate author and subject indexes. Fifty-six tables and seventy-four figures enrich the work.

An amazing mass of data is included in this volume; they make it a reference book rather than a text-book. The author shows a keenly critical spirit in his treatment of a very wide literature. The three volumes together constitute a unique and comprehensive account of general inorganic colloid chemistry and they should certainly be found in the library of all who are concerned with the laboratory

or technical study of colloid systems. Probably no one is better qualified than Professor Weiser to deal with this particular aspect of colloid chemistry because of his own original investigations over many years.

The volume, like its predecessors, is excellently printed and bound, and in view of its character is not expensive. The reviewer recommends it without hesitation.

WILLIAM CLAYTON

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Vol. XVIII. Editor: REYNOLD C. FUSON. Pp. v + 103. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1938. Price 8s. 6d. net.

For eighteen years now, with unfailing regularity, a volume of organic syntheses has appeared, and still there seems to be no diminution in the quality or quantity of the matter contained in this latest volume. As was to be expected, the original arrangement of subject matter, having been found satisfactory, is maintained without alteration.

Volume XVIII contains details for the preparation of twenty-nine compounds; a representative selection of these is as follows:—acetylene dicarboxylic acid, barbituric acid, α-chloroanthraquinone, 4 : 4-difluorodiphenyl, diphenylselenide, methyl benzyl ketone, 1 : 2-naphthalic anhydride, *l*-histidine monohydrochloride, 2-phenyl pyridine and taurine. In addition to the variety indicated above, several excellent examples of general reactions, such as the hydrolysis of a dioxymethylene group to a dihydroxy compound (the example chosen is the conversion of piperonal into protocatechualdehyde) are given. The preparation of Girard's reagent is also of special interest.

The volume closes with a list of later references to preparations recorded in previous volumes and also a list of additions and corrections. In this connection a special note on a simple and cheap preparation of methyl iodide in 90–94 per cent. yield is of considerable value and interest. The index covers Volumes X to XVIII.

The volume under review is more than usually interesting, for it covers a very wide range of compounds and may be commended to the notice of teachers of organic chemistry, organic research workers and manufacturers of fine chemicals.

HAROLD TOMS

QUALITATIVE ANALYSE MIT HILFE VON TÜPFEL-REAKTIONEN. Third Edition. By FRITZ FEIGL. Pp. 554. Leipzig: Akademische Verlagsgesellschaft m.b.H. Price RM.28.

A considerable amount of progress has been made in the theory and practice of spot test analysis since the publication of the second edition of this book in 1935 (*cf.* ANALYST, 1935, **60**, 205). Although the 1938 edition contains approximately the same number of pages, it has been completely revised, and its scope extended; this has been made possible by the omission of unimportant details and the condensation of the text to essentials.

The theoretical section contains much new material dealing with the chemistry of specific reactions and the effectiveness of organic compounds for spot tests in

relation to various groupings. An entirely new chapter containing a wealth of references, deals with the use of ultra-violet light in spot analysis.

Section II of the book has been entirely re-arranged in order to provide room for new material. The more obvious simple tests, such as potassium chromate for silver, are not described in detail, but adequate references are given. Details for the preparation of the organic reagents are also omitted in this edition, but again, references are provided. For the first time spot tests appear for indium, gallium, caesium and lithium. The detection of characteristic organic groups is a most useful application of spot-test technique. This has been amplified and new tests are given for α-amino acids, pyrrole derivatives, aromatic meta-dinitro compounds and oximes.

The technical section contains many new tests of great interest and utility. A typical example is the detection of tetra-ethyl lead in fuels.

Dr. Feigl is to be congratulated on further enhancing the value of a book which is already well established as the most authoritative and comprehensive in the field of qualitative micro-analysis. W. F. STEPHENSON

AGRICULTURAL ANALYSIS: A HANDBOOK OF METHODS EXCLUDING THOSE FOR SOIL. By C. HAROLD WRIGHT, M.A., F.I.C. Pp. 343. London: Thomas Murby & Co. 1938. Price 16s. net.

The title should convey that the book deals exclusively with methods of analysis of materials used or produced by the farmer, but excluding soils. The book does not contain information concerning the interpretation of results, but the authors have aimed at the production of a work to give those methods for the analysis of fertilisers, feeding stuffs, milk, milk products, insecticides and fungicides that should be useful to the agricultural analyst and student. In fact, the book is a laboratory manual, and the processes are based on the experience of the writer, who has been aided by many chemists well known for their research work.

Whenever possible the Official Methods of Analysis (Fertilisers and Feeding Stuffs Regulations, 1932) are quoted and given at length without comment. For many years now these methods have been in force in England and have become reverenced, perhaps from old age, so that no one seems ever to offer any drastic criticism concerning them. Perhaps it is as well that something that is English should be above suspicion and reproach. However, to the credit of the author, he does invariably give alternative processes that may be used when "official" determinations are not being made. But, apart from the actual processes, the book is valuable, because a chapter usually opens with an article which gives important information relative to the methods that follow. The article makes plain the process selected by the author as most suitable, gives information concerning the steps therein involved, or perhaps deals with the research which led up to the presentation of the final process. At all events, these preambles produce an atmosphere which tends to make the analytical procedure more understandable and, in some instances possibly, the process more easy to work.

The preparation of a sample of a fertiliser is dismissed in less than two pages; in fact, information is restricted to the reproduction of the British Official Method and that of the A.O.A.C. of America. Whilst it may be difficult to write on the

methods used for rendering a sample sufficiently fine to pass a 1-mm. sieve, the importance of making certain that the sample to be analysed represents the bulk should always be emphasised. To-day, when there are so many experienced chemists and when so many accurate processes are available, the probability of errors due to sampling always requires serious attention. Differences in results obtained in different laboratories to-day are usually the result of bad sampling rather than of bad analytical procedure. However, efficient sampling is usually the outcome of individual experience and it is, therefore, difficult to commit to paper the ways and means of sampling, especially as the condition of a commodity largely governs the treatment.

In succeeding chapters methods are given for the determination of nitrogen, phosphorus, potassium and calcium in various fertilisers, one-third of the book space being allotted to these elements. In the early pages the author directs attention to the use of selenium in the Kjeldahl process, but subsequently no general laboratory method embodying its use is given. One hundred pages are then devoted to the analysis of feeding stuffs, and the processes given in detail deal with both organic and inorganic constituents.

The chapter on milk products contains very recent information, for under butter the procedure recommended by the Society's Analytical Methods Committee in 1936 is given.

The literature of various countries has been well considered in the final section of the book, which deals with insecticides and fungicides. Herein have been included analytical methods for the examination of both derris and pyrethrum.

The processes given do not call for criticism because they are invariably those which have been accepted either in this country or elsewhere, but it must be remembered that a process has a limit of application.

The book should form a useful laboratory companion to those engaged in the analysis of agricultural materials. F. W. F. ARNAUD

EXPLOSIVES, MATCHES AND FIREWORKS. By J. REILLY, D.Sc. Pp. 172. London: Gurney & Jackson. 1938. Price 7s. 6d.

This work is to form part of Volume IV of the second edition of Lunge and Keane's Technical Methods of Chemical Analysis, which is now in the press. It has, however, been decided to publish this portion as a separate book.

The layout follows closely that of the corresponding portion of the 1911 edition of Lunge and Keane. A considerable enlargement has been made in the section dealing with explosives, but the amount of space devoted to matches and fireworks is almost identical with that in the earlier edition, very little revision having apparently been attempted in these subjects.

The explosives section is divided into three portions; the first describes the properties and tests of ingredients and raw materials; the second deals with the analysis of explosives and the third with stability tests. A somewhat similar subdivision is adopted with matches and fireworks so far as this is possible, namely, raw materials, finished products and tests.

The most serious defect of the work is the disproportion in allotting space to the various subjects. Thus nitroglycerin is dismissed in a few lines, whilst glue,

described under binding substances for matches, receives no less than sixteen pages. Again, physical and explosive tests of explosives are disposed of in six pages, of which *less than one* deals with sensitiveness to shock and friction. There is also an unnecessary overlap, mercury fulminate being described among explosives and again under fireworks.

It is regrettable that in describing certain substances, as, for example, acetone and ether, for which British Standard Specifications are available, no mention is made of this fact.

In one or two instances errors have been reproduced from authorities referred to. Thus the melting point of Centralite I, which is 72° C., is given as 79° C., this error having been repeatedly reproduced since its first publication by Michler in 1876. Again, Ball's method of determining sodium follows an erroneous description given in *Industrial and Engineering Chemistry*, 1920, **12**, 576.

More attention might well have been given to the methods for confirming the identity of nitrocellulose and of nitroglycerin in view of the fact that these substances are the bases of so many explosives. The melting-point of nitroglycerin is mentioned as being sometimes used as a criterion of purity. It is thought that such a statement should be accompanied by a warning as to the extreme sensitiveness of this substance when in a semi-molten condition. No mention is made of the value of the refractive index as a means of its identification.

The book is well printed in very readable type on good paper, and its accuracy is generally high. It will prove most useful to those wishing to refer to a concise account of the tests for the products described and the ingredients used in their manufacture. Those called upon to carry out detailed examinations will be obliged to seek information in the more comprehensive works, of which there is a useful bibliography. Reference is freely made to original literature and the work is also well indexed.

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FLUORESCENZ-MIKROSKOPIE. By MAX HAITINGER. Pp. viii + 108 + 4 plates. Leipzig: Akademische Verlagsgesellschaft m.b.H. 1938. Price RM.10.80.

It is not long since fluorescence analysis in ultra-violet radiation was regarded as a highly-specialised branch of chemical analysis, and it is possibly a sign of the times that this branch should now begin to develop even more highly-specialised off-shoots of its own. The present volume deals with one of these, and, incidentally, the third which has been the subject of a book within the past year. However, it is none the less a welcome contribution to the literature of chemical analysis, partly because, in the reviewer's opinion, at any rate, fluorescence microscopy is a method which has considerable latent possibilities, and partly because the author is one of the foremost authorities on the technique of the subject, even if most of his applications of the method have been histological rather than chemical in nature.

Fluorescence microscopy is the use of the microscope with filtered ultra-violet light substituted for the visible light normally used as an illuminant. As with ordinary microscopy, the object may be viewed either by transmitted light or by incident (reflected) light. Each method has its advantages, the determining factor being usually the nature of the specimen, but the former requires special microscope equipment, whilst so long as a suitable source of ultra-violet light is

available an ordinary microscope may be adapted to the latter with little trouble or cost.

The author purposely avoids dealing with the nature and production of ultra-violet light and fluorescence effects in general, and passes immediately to descriptions of apparatus of the above-mentioned types, particular attention being given to the nature of the source, a matter of which he has made a special study. The reviewer has obtained good results with one of the new types of mercury vapour lamps in the form of an almost point-source, but Haitinger considers that an iron arc ensures the best results, and if one may judge by the photographs which illustrate the book, there is a good foundation for this claim.

The primary fluorescence of the preparation as seen under the fluorescence microscope frequently enables fluorescent structures (*e.g.* containing starch or fat) to be seen, which in ordinary light are invisible or indistinct, even after staining. The scope of the method, however, may be increased still further by treatment of the specimens with substances which are analogous to the usual microscope stains except that they fluoresce characteristically when in contact with certain structures. These are known as "fluorochromes," and, as their application to histological work has been a special study of the author, it is not surprising that they are given precedence, so far as space is concerned. A valuable feature of the book, therefore, is two tables in which the properties, fluorescence, optimum concentrations and staining-periods of some 23 of such fluorochromes are summarised in relationship to their uses for the distinction of substances and structures such as cell nuclei, protoplasm, mucilage, collagen fibres, fat, starch, membranes, and so on. Details are given of the specialised technique required for the preparation and mounting of the specimens. Interesting recent developments which are also dealt with are the formation of fluorochromes *in situ* (*e.g.* by the diazo reaction) and the use of more than one fluorochrome—a procedure analogous to multiple-staining in ordinary microscopy.

Needless to say the book abounds in examples of the applications of the method. Most of these are drawn from the author's own work and therefore, are mainly histological in nature (*e.g.* the examination of cell membranes, protein, crystals, connective and supporting tissues, and investigations on bacteria and viruses). These are illustrated by about 30 excellent photographs in black and white; the author, feeling no doubt the inevitable inadequacy of reproductions of this kind, has, however, also included 6 colour-photographs which, if one makes allowance for the subtle nature of differences in fluorescence, can only be regarded with admiration.

The salient features of the literature of the chemical and technical applications of the method are also summarised (7 pages), and the book concludes with a classified bibliography of 168 items and the usual indexes. It may be recommended warmly to all interested in this new technique; in fact, the only point open to criticism is its price which, even if one makes allowance for the coloured plates, is rather high for a book containing less than 100 small pages of actual text in a paper cover.

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