JUNE, 1928. Vol. LIII., No. 627.

THE ANALYST

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

AN Ordinary Meeting of the Society was held in the Chemical Society's Rooms, Burlington House, on Wednesday, May 2nd, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of Bhagwat Prasad Bhargava, B.Sc., Cyril Ernest Gill and Thomas Percy Hilditch, D.Sc., F.I.C.

Certificates were read for the second time in favour of:—Arthur Duncan Gay, John Gordon Mayne, Reginald Arthur McNicol, M.Sc., A.I.C., William Ramsden Orrell, B.Sc., A.I.C., Laurence Frederick Smith, M.Sc., A.R.C.S., Dipl. Imp. Coll., A.I.C., Charles Frederick Turner, F.I.C.

The following were elected Members of the Society:—Frank Rowland Hill, B.Sc., A.I.C., Edward Thomas Illing, B.Sc., F.I.C., Farid Iskander, Harry Bulmer Marston, B.Sc., A.I.C., Reginald James Munro, B.Sc., A.I.C., John Ralph Nicholls, B.Sc., F.I.C., H. Gordon Reeves, D.Sc., Ph.D., F.I.C., George Walsh, B.Sc., A.I.C., Ronald George Warren, B.Sc., William Arthur Waygood, B.Sc., A.R.C.S., A.I.C.

The following papers were read and discussed:—"Locust Kernel Gum and Oil," by A. L. Williams, A.I.C. (work done under the Analytical Investigation Scheme); "The Separation of Lead Tetra-Ethyl from Solution in Petroleum Spirit," by F. W. Toms, F.I.C., and C. P. Money, B.Sc., A.I.C.; "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates. XII. Observations on the Pyrosulphate Hydrolysis Method," by W. R. Schoeller, Ph.D., and E. F. Waterhouse; "A New Precipitation Method for the Determination of Vanadium, and its application to Steel Analysis," by B. S. Evans, Ph.D., F.I.C., and S. G. Clarke, B.Sc., A.I.C.; "Methods for the Analysis of Liquorice Mass," by P. Houseman, Ph.D., F.I.C.; and "The Use of Mitchell's Ferrous Tartrate Reagent in Studying the Precipitation of Alkaloids by Tannin," by A. E. Jones, B.Sc., A.I.C. (work done under the Analytical Investigation Scheme).

Obituary.

BENEDICT KITTO, F.I.C.

WITH the death of Benedict Kitto, which took place on May 13th, at the age of 87, there leaves our number one who has not only filled the position of Public Analyst for the County of Cornwall for forty years, but has also been a prominent exponent of mineralogy, geology, mining and assaying for a still longer time.

He was elected a member of the Society of Public Analysts in February, 1892, served on the Council during the years 1895–96, and was Vice-President in 1905–6.

Benedict Kitto was born in 1841 at Breage in Cornwall. After a private education he received his professional education at the Royal College of Science and the Old College of Chemistry. Following many years of lecturing on mining subjects in Cornwall, in 1881 he succeeded J. H. Collins as Public Analyst for the County of Cornwall, but resigned the following year to become Chief Chemist in London to the Rio Tinto Mining Company, where he continued till 1887, when he commenced private practice in St. Swithin's Lane. In 1892 he was re-appointed Public Analyst for the County of Cornwall, this time succeeding Mr. Beringer. He became a Fellow of the Institute of Chemistry in 1888.

While Mr. Kitto's attainments as a Public Analyst were conspicuous, and he enjoyed the confidence and esteem of his fellow Public Analysts, there was concurrently another side of his professional life which others have greatly appreciated. He had a first-hand knowledge of Cornish and Devon mines and also of many in Wales, Spain and Portugal, and had a great repute as mineralogist and assayer. He was a Fellow of the Geological Society, an Associate of the Royal Geological Society of Cornwall, a member of Council of the Mineralogical Society, and a Founder-member and Honorary Member of the Institution of Mining and Metallurgy. He was Examiner in Assaying to various bodies, including the Cornwall County Council and the Mining Schools of Camborne, Redruth, and Penzance.

His personal qualities were admirable. It was ever a satisfaction to meet him; his unfailing tact and kindness were the inevitable manifestations of a kindly nature which remained unchanged and unalloyed through a long strenuous life.

His wife predeceased him by forty-three years, and he leaves two sons and a daughter.

WILLIAM PARTRIDGE.

Behaviour of Indicators in the Titration of Ammonia, Sodium and Calcium Phosphates, the Methylamines, Pyridine Bases and Boric Acid.

By R. T. THOMSON, F.I.C.

(*Read at the Meeting, March* 7, 1928.)

In recent years indicators have been studied mainly from the point of view of P_H value, but this does not always show their value for the practical analysis of commercial articles, although it is sometimes regarded as if it did. For example, as will be seen later, brom-phenol blue has a range about the same as methyl orange, but it fails to give accurate results in the determination of free acid in ammonium sulphate. It is thus imperative to determine the suitability of each indicator for the particular purpose to which it is to be applied, and to take its P_H value as an indication of what it may probably accomplish.

I. Ammonia.—In the following table are given the results, with different indicators, of the titration of pure ammonium sulphate, 2 grms., dissolved in 100 c.c. of water, being used:

Table I. Behaviour of Indicators with Ammonium Sulphate.

	Alkalinity as NH_3. Per Cent.	Acidity as H_2SO_4. Per Cent.	Colour change.
Brom-phenol blue ..	0·12	alkaline	fair
Methyl orange	neutral	neutral	distinct
"Sofnol" No. 1	neutral	neutral	distinct
Methyl red	neutral	neutral	distinct
Brom-thymol blue ..	neutral	neutral	fair
Phenol red	acid	1·3	obscure
Naphtholphthalein ..	acid	1·2	obscure
Cresolphthalein	acid	1·6	obscure
Phenolphthalein	acid	1·8	obscure
Phenol violet	acid	1·8	obscure
Thymol violet	acid	5·2	obscure

Where there is any carbonic acid present, all these indicators are of no value in the titration of ammonia, except methyl orange and brom-phenol blue, and the latter must also be ruled out, owing to its alkaline reaction with neutral ammonium sulphate. An important question in this connection is the determination of free acid in commercial ammonium sulphate, the neutral variety of which must not contain more than 0·025 per cent. of free acid, calculated as H_2SO_4. To determine this it is necessary to use from 20 to 25 grms. of the sample; and for 20 grms. of ammonium sulphate, purified by recrystallisation, 0·4 c.c. of 0·1 *N* sulphuric acid was required to show a distinct change in colour with methyl orange, which is equal to 0·008 per cent. of sulphuric acid. In determining free acid in this

way, the error might amount to 0·003 to 0·005 per cent. on the low side, so that, if carefully tested, a high result would not be obtained. In a similar test with an ammonium sulphate containing 0·013 per cent. of sulphuric acid, with bromo-phenol blue as indicator, 10 c.c. of $N/10$ sodium hydroxide solution were required before the yellow colour was reached, but the violet changed so slowly that the end-point change was very obscure. From these results it is apparent that ammonium sulphate may contain 0·3 per cent. of free sulphuric acid before it could be said to be acid to this indicator. A sample of ammonium sulphate containing 0·010 per cent. of free sulphuric acid showed 0·025 per cent. with Sofnol No. 1, when 20 grms. were employed for the test.

If ammonium sulphate contains any ferric sulphate, about half of the SO_3 would be returned as free acid when methyl orange is used as indicator, but ferrous sulphate remains neutral, and has no appreciable effect on the colour change. With methyl red, practically the whole of the SO_3 would be determined in ferric sulphate, but in ferrous sulphate not more than 0·1 per cent. of the SO_3 would be estimated, so that it may be regarded as neutral. To bromo-phenol blue, ferric sulphate is acid to some extent, but ferrous sulphate is distinctly alkaline.

Taken all round as an indicator for the determination of ammonia, and for the acidity or alkalinity of ammonium salts, there is no indicator that can take the place of methyl orange with advantage. When there is no carbonic acid present, methyl red will give a more delicate and rapid change of colour at the neutral point, but bromo-phenol blue is useless, although it has been recommended.

II. Phosphates of Sodium and Calcium.—In the following table are given results of the titration of different phosphates of sodium, the figures being the proportion of Na_2O on 100 parts of that ingredient present.

Table II. Behaviour of Indicators with Phosphates of Sodium, showing Percentage of Na_2O determined.

	Na_2HPO_4.	NaH_2PO_4.	End-point.	$Na_4P_2O_7$.	$NaPO_3$ or $Na_2H_2P_2O_7$.	End-point.
Bromo-phenol blue	52	alkaline	fair	52	alkaline	fair
Methyl orange	50	neutral	distinct	50	neutral	distinct
Methyl red	43	acid	obscure	43	acid	obscure
Bromo-thymol blue	40	acid	obscure	40	acid	obscure
Phenol red	5	acid	obscure	26	acid	obscure
Naphtholphthalein	4	acid	obscure	25	acid	obscure
Cresolphthalein	neutral	acid	distinct	12	acid	obscure
Phenolphthalein	neutral	acid	distinct	12	acid	obscure
Phenol violet	neutral	acid	distinct	12	acid	obscure
Thymol violet	acid	acid	fair	3	acid	fair

The acidity shown by thymol violet is equal to about 3·5 per cent. of disodium hydrogen phosphate.

These tests were made on pure Na_2HPO_4 and on $Na_4P_2O_7$ prepared from it, and the $NaPO_3$ and $Na_2H_2P_2O_7$ were also prepared specially. It will be observed that, while the alkalinity of the pyrophosphate corresponds to that of the dibasic phosphate when bromo-phenol blue, methyl orange, methyl red or bromo-thymol blue are used as indicators, a large increase is shown with all the other indicators.

This peculiarity becomes of importance when a sample of commercial acid pyrophosphate or metaphosphate of sodium is to be tested for acidity. It is evident that a direct titration, with phenolphthalein or phenol violet as indicator, will not give a true result for acidity, as it will be much too low. Thus, a sample of acid pyrophosphate of soda gave only, as near as could be judged, 80 per cent. of the pure substance, whereas it contained 95 per cent. It follows from this that it would be necessary to hydrolyse by boiling with an acid before titrating. It was found that by boiling 100 c.c. of a solution containing 1 grm. of the substance and 10 c.c. of normal nitric, hydrochloric or sulphuric acid, for 15 minutes, the result was only 90 per cent. With 30 minutes' boiling, the full percentage was obtained, but it is preferable to add excess of nitric or hydrochloric acid to the solution, evaporate to dryness, and thus get rid of the excess of added acid. The residue is then dissolved in cold water, made neutral to methyl orange, and titrated with standard caustic soda, phenolphthalein being used as indicator. It is necessary also to test the original sample as to whether it is alkaline or acid to methyl orange, and to determine the amount of either of these. If alkaline, the equivalent in acid phosphate must be subtracted from the result, and if acid it must be added. It should be noted that in titrating phosphates the quantity of phenolphthalein used should be limited as much as possible.

Another article of commerce which, like acid sodium pyrophosphate, is used as the acid principle of baking powders, is acid calcium phosphate. The acidity of this substance towards sodium bicarbonate is difficult of proof, and does not appear to have been satisfactorily demonstrated. Of the methods in use, two, which depend on titration with standard sodium hydroxide solution, require the use of phenolphthalein as indicator. In one of these 1 grm. of the sample is titrated in a solution of 4 grms. of sodium chloride in 30 c.c. of water till a pink colour appears, then heated and the titration continued. In the other, by H. Adler and G. E. Barker (*Cereal Chemistry*, Nov. 1925, page 389), 0·84 grm. of the sample is treated with 25 c.c. of water, 90 c.c. of 0·1 *N* sodium hydroxide solution added, boiled for one minute, and titrated with 0·2 *N* hydrochloric acid until the pink colour has almost disappeared. It is now boiled again for one minute and the titration finished. Trials were made with a sample of acid calcium phosphate, of which the following is a complete analysis:

Soluble in water.	Per Cent.
Acid calcium phosphate ($CaH_4P_2O_8$)	46·65
Acid magnesium phosphate ($MgH_4P_2O_8$)	0·64
Free phosphoric acid (H_3PO_4)	0·10
Calcium sulphate	2·48
Combined water	7·99
Moisture (loss at 100° C.)	4·05
Insoluble in water.	
Dicalcium phosphate ($Ca_2H_2P_2O_8$)	23·07
Calcium fluoride	0·31
Ferric phosphate	0·77
Silica	0·16
Combined water, etc.	13·78
	100·00

The combined water, etc., in the substances insoluble in water contained a minute quantity of organic matter.

Assuming that tribasic calcium and magnesium and disodium phosphates are formed during titration, the following should be required for 1 grm. of the sample:

	0·1 *N* sodium hydroxide solution. c.c.
Phosphates soluble in water	54·1
Phosphates insoluble in water	11·3
Total phosphates	65·4

Both of the methods described above were applied to this sample, the results being as follows:

	0·1 *N* sodium hydroxide solution.		
	Soluble portion. c.c.	Insoluble portion. c.c.	Total. c.c.
First method	56·5	12·5	69·0
Second method ..	57·6	13·7	71·3

It will be observed that the result by the first method described above is 3·6 c.c. too high, and by the second method 5·9 c.c. too high.

These differences cannot be ascribed to the decomposition of calcium sulphate by sodium carbonate in the standard sodium hydroxide, as there was only 1 c.c. of its alkalinity in 100 c.c. due to this, whereas the calcium sulphate in the sample would require 3·6 c.c. Tests were next made to ascertain the effect of sodium hydroxide on tribasic calcium phosphate, but it is a difficult matter to prepare the latter in a state of purity. To obviate this, enough lime water, carefully tested for its alkalinity, was added to a quantity of the water-soluble portion of the acid calcium phosphate sample, so that it would contain the same amount of tribasic calcium phosphate as 1 grm. of the soluble part of the sample. To this was added 10 c.c. of 0·1 *N* sodium hydroxide solution, and the liquid boiled for one minute, and titrated back with standard acid, when it was found that 2·5 c.c. of the sodium hydroxide solution had been neutralised, and sodium phosphate had gone into solution. It is evident from this result that the tricalcium phosphate had been rendered more basic by the sodium hydroxide, and there could be no decomposition of calcium sulphate, as there was practically no sodium carbonate in the 10 c.c. of sodium hydroxide solution.

Trials were made to determine what results would be obtained by titration of acid calcium phosphate with sodium carbonate. Working on 1 grm. of the sample, 25 c.c. of 0·5 *N* sodium carbonate solution were added, the liquid boiled, filtered, and a double titration of the filtrate made, methyl orange and phenolphthalein being used as indicators. In another test the mixture was evaporated

to dryness, the residue treated with water, filtered, and the filtrate titrated as before. The results were identical:

	0·1 *N* sodium hydroxide solution consumed. c.c.
Soluble portion	62·5
Insoluble portion	19·0
Total	81·5

These results are still higher than those obtained by the use of sodium hydroxide, but 3·6 c.c. must be subtracted for the decomposition of calcium sulphate, which gives 77·9 c.c. for the phosphates alone. A tricalcium phosphate precipitate, prepared as described above, was decomposed to some extent when boiled with sodium carbonate, sodium phosphate going into solution, while the precipitate had the following composition:

	Per Cent.
Tricalcium phosphate	88·6
Calcium carbonate	11·4
	100·0

This decomposition of tricalcium phosphate by sodium carbonate will, in the main, account for the high results, but the ferric phosphate may also be decomposed.

When heated with solution of sodium carbonate, the insoluble matter from the sample of acid calcium phosphate did not liberate carbonic acid until the temperature rose to about 100° C., and quantitative tests were made in a carbonic acid apparatus, excess of sodium carbonate being used. The temperature was kept just under the boiling point till action ceased, and it was found that the carbonic acid expelled corresponded with the formation of tricalcium phosphate and disodium phosphate.

It is apparent, from the above results, that the first method of analysis will give results about 5 per cent., and the second method 9 per cent., too high in acidity of acid calcium phosphate towards sodium carbonate or bicarbonate, this being an unfair comparison with the acidity of cream of tartar.

In the *Chemical News* for 1884 (Vol. **49**, p. 39), I showed that if acid calcium phosphate is titrated with sodium hydroxide solution in presence of excess of calcium chloride, a high result is obtained, owing to the production of a basic phosphate. This occurs also in the two methods examined, where there is no excess of calcium compounds, so that it will be a difficult matter to find a titration method that will give correct results, and, so far, further tests have failed to show in what direction an accurate method can be found.

III. The Methylamines.—The behaviour of indicators with mono- di- and tri- methylamine is exactly the same as with ammonia, and methyl orange is the best indicator when carbonic acid is present.

It may be of interest to give the result of trials which were made with the object of determining ammonia and the three methylamines which were produced and vaporised during the drying of fish. In this case Nessler's reagent may be regarded as an indicator in the testing of these, as well as for determining the proportion of each. In comparatively strong solutions these substances give precipitates with Nessler's reagent, but, in very dilute solutions, ammonia, monomethylamine and dimethylamine give the same colour, but of different intensities when the same amount of each is present. Trimethylamine gives no reaction with Nessler's reagent in such dilute solutions. It was found that standard ammonium chloride could be used in determining mono- and di-methylamine, and that the proportions of each, equal to 1 c.c. of ammonium chloride of a convenient strength, are represented as follows:

	1 c.c. of NH_4Cl solution represents Mgrm.
Ammonia	0·10
Monomethylamine	0·85
Dimethylamine	10·60

If nothing but the four substances is present in a solution, the total alkalinity is determined by standard hydrochloric acid, the liquid evaporated to dryness, and the mixed chlorides weighed. These are now triturated with chloroform, filtered, the filtrate evaporated, and the residue dried at 100° C., and then weighed, the result giving dimethylamine and trimethylamine chlorides. These are dissolved in a convenient quantity of water, and a portion tested for dimethylamine by Nessler's reagent, from which result both of the chloroform-soluble methylamines can be calculated. In a similar manner the ammonia and monomethylamine may be determined in the substance insoluble in chloroform, but where the former is largely in excess of the latter, the determination cannot have the same accuracy as with the portion soluble in chloroform.

The liquid condensed from the drying of fish had to be distilled into an excess of hydrochloric acid, evaporated, and the chlorides weighed. In weighing these, it should be kept in view that di- and tri- methylamine chlorides are deliquescent, and may absorb as much as 60 per cent. of water from the atmosphere. Trimethylamine chloride is very soluble in chloroform, but 100 c.c. of this solvent only dissolves about 1 grm. of dimethylamine chloride.

The proportions of the products in the condensed water from the drying of whiting was as follows:

	Fresh fish. Per Cent.	Decomposed fish. Per Cent.
Trimethylamine	0·041	0·063
Dimethylamine	0·006	0·009
Ammonia and monomethylamine ..	0·062	0·096

No definite result was obtained by testing the last two substances, as the proportion of monomethylamine was very small.

IV. PYRIDINE BASES.—Ordinary commercial pyridine was tested for alkalinity with different indicators, the result with Congo red being taken as 100 per cent.

	Alkalinity. Per Cent.
Congo red	100
Bromo-phenol blue	101
Methyl orange	99
Methyl red	40
Phenol red	25
Phenolphthalein	0·5

With thymol violet the reaction of pyridine was acid, to the extent of the equivalent of 0·24 per cent. of sulphuric acid, and the end-point of the reaction was fairly good. With the other indicators none of the end-point changes in colour was very good, except with phenolphthalein, which was fairly satisfactory.

BORIC ACID.—Sofnol No. 1 has been recommended for the same purpose as methyl orange, but it is really seriously affected by carbonic acid, so that it cannot be used as a substitute except in special cases. Scott Dodd (ANALYST, 1927, **52**, 464) recommends "Sofnol" No. 1, in place of methyl orange, as an indicator in obtaining the neutral point in boric acid solutions, carbonic acid being absent. It is certainly preferable, under the conditions in which he was working, *viz.* the absence of carbonic acid and the presence of only small proportions of boric acid. Up to 0·2 grm. of boric acid per 100 c.c. of solution the change in colour is fairly good, but such a solution gives a perceptible acid reaction to Sofnol No. 1. A solution containing 1 grm. of boric acid per 100 c.c. gave a very distinct acid reaction, and consumed 0·5 c.c. of 0·1 *N* sodium hydroxide solution to bring it to the neutral point. Where larger quantities of boric acid than 0·2 grm. are being titrated, methyl orange is to be preferred.

The Determination of Butter in Margarine.

By L. V. COCKS, A.I.C., and E. NIGHTINGALE, A.M.C. Techn.

(*Read at the Meeting, February* 1, 1928.)

Discordant results, which have been obtained by different analysts in the determination of butter in amounts up to 10 per cent. in margarine by the Reichert–Meissl, Polenske and Kirschner values, and subsequent interpretation from these figures, have led to a critical and detailed investigation of this method.

The technique adopted for carrying out the practical determinations has been based on that described by Bolton and Revis (Analyst, 1911, **36**, 335), while the formulae and graphs proposed by Bolton, Richmond and Revis (Analyst, 1912, **37**, 183) have been employed for calculating the amounts of butter present in admixture.

Practical Investigation.—The first essential feature in the determination of butter by the Reichert–Meissl, Polenske and Kirschner value method was that good agreement should be invariably obtained when duplicate tests were made by one, or by several analysts. Even after every allowance had been made for an operator to become perfectly familiar with the details of the procedure, in which practice is essential, certain variations in the results were still observed.

Other workers (Elsdon and Smith, Analyst, 1925, **50**, 53) have apparently encountered similar difficulties. Consequently a careful study of each stage of the determination was undertaken, with the result that, when a latitude for reasonable deviation from the details given by Bolton and Revis was provided for, no one particular feature mentioned by them could be found responsible for the discrepancies. In addition to attention being paid to the points emphasised by previous investigators, namely, the preparation of the fat, the completeness of saponification without decomposition, the size of the powdered pumice, the dimensions of the apparatus, the temperature of the cooling water, and the time of distillation, the necessity for using perfectly pure and finely powdered silver sulphate was made evident. With silver sulphate of inferior quality low Kirschner value figures were obtained.

In addition, on occasions, traces of sulphuric acid were detected in the Kirschner distillate, and from a large series of experiments, in which many "blank" distillations, pure butyric acid distillations, and normal tests on different fats were carried out, the presence of sulphuric acid in the Kirschner distillate was definitely found to be associated with an asbestos shield which did not fit the bottom of the distillation flask in a perfect manner. A Joint Committee of the Government Laboratory and the Society of Public Analysts, appointed for the

standardisation of the Reichert–Wollny Process, stated that the distillation flask should be protected by a piece of asbestos, 12 cm. in diameter, with a central hole, 5 cm. in diameter, and that care should be taken not to heat the asbestos itself.

No mention, however, appears to have been made of the essential point, that the asbestos should fit perfectly. During use, an ordinary well-fitting asbestos shield will become uneven and worn away, with the result that very small annular spaces will be left between the shield and the flask. Such spaces are quite sufficient to enable the hot gases, playing on the walls of the flask, to volatilise sulphuric acid during the determination of the Kirschner value, even though the gas flame is definitely directed towards the bottom of the flask.

The amount of sulphuric acid which can thus pass into the distillate in the Kirschner determination was found to be as follows:

	Asbestos Shield.		
	Perfect fit. *N*/10 NaOH. c.c.	Small annular space. *N*/10 NaOH. c.c.	Difference due to sulphuric acid. *N*/10 NaOH. c.c.
Blank control	0·04	0·60	0·56
Blank with pure butyric acid	2·71	3·35	0·64
Coconut oil	2·15	2·71	0·56
Hydrogenated whale oil ..	0·45	0·98	0·53

In the above series the annular space, although small, was definite. When the size of the space was reduced, the quantity of volatilised sulphuric acid became less. Thus, if the asbestos shield fitted defectively in one place only, the amount of sulphuric acid in the distillate corresponded to 0·10 to 0·20 c.c. of *N*/10 solution.

A satisfactory, well-fitting and reasonably permanent shield was made from Uralite plate (asbestos and cement), the central hole of which (5 cm. in diameter) was cut in a bevelled fashion, so that the walls at the bottom of the flask fitted closely into the hole. The final joint was made with asbestos paper with a central hole of slightly less diameter than 5 cm., on to which the flask was firmly clamped. When a shield of this type was used no sulphuric acid passed into the Kirschner value distillate.

Experiments showed that in the Reichert–Meissl and Polenske distillation no sulphuric acid was volatilised, even if a small annular space existed between the flask and the shield, but that under such conditions there was a tendency for the Polenske value to be too high. The non-volatility of the sulphuric acid is probably connected with two factors, *viz.* (1) the presence of fatty acids on the walls of the flask, and (2) the presence of a smaller excess of sulphuric acid than in the Kirschner determination, in which there is an excess of at least 8 c.c. of a 5·3 per cent. sulphuric acid solution, whilst in the Reichert–Meissl, Polenske determination the excess is only 5 c.c. of a like solution. The following blank Kirschner tests demonstrated that the amount of sulphuric acid which distilled over when an

annular space existed between the flask and the shield, varied with the excess present:

Excess of 5·3 per cent. sulphuric acid. c.c.	Titration of the distillate, $N/10$ NaOH. c.c.
1	0·12
3	0·30
5	0·50
7·5	0·75
20	1·90

Attempts were made to reduce the excess of 5·3 per cent. sulphuric acid solution to 1·0–2·0 c.c. in the Kirschner value determination, but in such cases it was found that slightly less than the normal amount of the volatile fatty acids passed into the distillate.

It was concluded, therefore, that, in order to obtain reliable and consistent results, the details given by Bolton and Revis (*loc. cit.*) must be adhered to, and, in addition, a perfect fit between the 5 cm. hole in the shield and the flask must be ensured. By adopting this procedure and testing each Kirschner distillate for sulphuric acid, it has been found possible to eliminate almost entirely the discrepancies between duplicate determinations of the Reichert–Meissl, Polenske, and Kirschner values, made by the same and by different operators.

INTERPRETATION OF RESULTS.—With satisfactory agreement established in the practical portion of the determination, attention was directed to the interpretation of the figures obtained. It seems to be generally agreed that the Kirschner value is directly proportional to the amount of butter present (see Bolton, Richmond and Revis, and Elsdon and Smith, *loc. cit.*). Apparently for the compilation of the tables, formulae and graphs, the most usually accepted Kirschner value figure for butter fat has been 23·5, although butter fats of 22·0, 24·2 and 24·8 have also been employed.

Many investigators have drawn attention to the fact that deviations from the average in the constants of the butter fat in admixture are liable to cause errors in the use of the formulae, but nowhere is the influence of such variations as are known to occur in genuine butter clearly shown. According to the literature, authentic butter fats have been encountered with Kirschner values ranging from 19 to 27, while to the knowledge of the authors there are on record butter fats, the adulteration of which is difficult to prove, with Kirschner values as low as 17. Moreover, in recent years, it has not been at all uncommon to receive large and continuous consignments of New Zealand butter fats with Kirschner values ranging from 20 to 20·5. The accurate determination from the standard formula or graphs of the butter content of mixtures, by an analyst who is ignorant of the Kirschner value of the butter fat originally incorporated, must therefore be considered problematical. Thus, if a butter fat of Kirschner value 20 had been used in a mixture, the results, as interpreted from formulae, graphs, or tables based on butter fats of Kirschner values 22·0, 23·5, 24·2, and 24·8 would require multiplying by 1·1,

1·175, 1·21, and 1·24, respectively; or, in other words, a reported figure of 8·0 per cent. of butter might really in an extreme case represent 9·9 per cent. Naturally, with smaller amounts of butter, the difference would become proportionately less. The significance of the Kirschner value of the butter fat is illustrated by the following quotations from actual determinations, the corrected figures being calculated on the assumption that Bolton, Richmond, and Revis used a butter fat of Kirschner value 23·5 for the compilation of their graphs:

		Analytical data of margarine mixture.			Butter, per cent. Interpreted from Bolton, Richmond and Revis's graphs.		
		Reichert–Meissl value.	Polenske value.	Kirschner value.	(*a*) Direct.	(*b*) After correction for Kirschner value of the butter fat used.	Actual amount added.
A.	New Zealand Butter Fat. (Kirschner value 20·2.)						
	1.	3·00	3·4	0·94	1·3	1·5	2·0
	2.	0·84	0·4	0·74	2·0	2·3	3·0
	3.	6·27	8·6	1·82	3·1	3·5	3·0
	4.	5·62	7·2	1·95	4·3	5·0	5·0
	5.	5·75	4·9	2·50	7·3	8·4	8·7
	6.	5·31	3·2	2·71	8·7	10·1	9·8
	7.	4·21	1·7	2·56	8·8	10·2	10·0
B.	New Zealand Butter Fat. (Kirschner value 20·5.)						
	8.	5·41	5·6	2·00	5·0	5·7	6·0
	9.	5·08	3·0	2·53	8·0	9·1	9·0
C.	New Zealand Butter Fat. (Kirschner value 24·2.)						
	10.	4·87	5·0	1·88	4·7	4·6	4·9
	11.	5·35	4·9	2·11	5·7	5·5	5·8
D.	English Butter Fat. (Kirschner value 22·4.)						
	12.	4·92	4·3	2·22	6·3	6·6	6·9
	13.	5·77	4·4	2·59	7·8	8·2	8·5
E.	Danish Butter Fat. (Kirschner value 23·7.)						
	14.	6·63	5·2	3·30	10·4	10·4	10·9

The results showed that the direct interpretation of the values, according to Bolton, Richmond and Revis's graphs, led to a distinct under-estimation in the case of the admixtures with the lowest Kirschner value butters, the widest divergence in the table being 1·4, or 19 per cent. on the butter. When, however, a correction was made for variations in the Kirschner value from 23·5, the estimated butter content agreed closely with the amount actually incorporated, as can be seen from a comparison of the figures in the last two columns.

The results have also been interpreted from formulae and tables given by

Elsdon and Smith (ANALYST, 1925, **50**, 53; 1926, **51**, 72; 1927, **52**, 63), and from those of Arnaud and Hawley (ANALYST, 1912, **37**, 122); but, even when corrected for variations in the Kirschner value of the butters, the figures are not quite so close to the actual values as those given by the formulae and enlarged graphs of Bolton, Richmond, and Revis. The procedure described by these authors must, therefore, be considered quite satisfactory for mixtures containing butter fat of the mean Kirschner value 23·5. Since, however, the accredited Kirschner value variation in butter fat is from 19 to 27, and the graphs are based on a butter fat of Kirschner value of approximately 23·5, the butter per cent. reported by an analyst who is ignorant of the Kirschner value of the butter fat in an unknown mixture may be as much as 13 per cent. too high or 24 per cent. too low, both figures being taken as a percentage on the actual butter content that would be read off from the graphs or tables. If 17 were considered as the extreme minimum for the Kirschner value of butter fat, then the possible under-estimation of the butter would be 38 per cent. Thus, with the usual limits of 19 to 27, an apparent 8 per cent. of butter might represent anything between 7 per cent. and 9·9 per cent. actual butter content, whereas, if 17 were adopted as the lowest Kirschner value for butter fat, an apparent 8·0 per cent. of butter might really represent 11·0 per cent. It may be mentioned that no butter fats of higher Kirschner value than 25 have been met with recently by the authors, and if 25 were taken as an upper limit the ranges would become 7·5 to 9·9 per cent., or 7·5 to 11·0 per cent.

None of the normal constituents of margarine has shown variations in Kirschner value that would account for appreciable error in interpreting the butter content of a mixture. The normal slight fluctuations in the Polenske value of the nut oils, and the incorrect allocation of coconut oil for palm-kernel oil or *vice versa*, would, according to the graphs, only result in small errors of the order of 0·2–0·4 per cent. of butter on the mixture. Misinterpretation of the figures due to the second cause should be somewhat remote, as the approximate determination of the relative amounts of these two oils should be an easy matter, either according to Blichfeldt (*J. Soc. Chem. Ind.*, 1919, 150T), or Elsdon and Smith (ANALYST, 1927, **52**, 63). Practical errors in the determination of the Polenske value of 0·5 units represent approximately 0·2 per cent. of butter.

A careful review of the literature has not revealed any more promising method of determining butter in admixture, since all processes are directly or indirectly dependent upon the acids of the butyric class, the amount of which is known to be variable in different butters.

SUMMARY AND CONCLUSION.—In the determination of butters, in amounts up to 10 per cent. in margarine, by the Reichert–Meissl, Polenske, and Kirschner processes, in conjunction with published graphs and formulae, discrepancies are found to occur between the results of individual analysts, all of which may differ from the actual amount of butter incorporated.

A critical survey of the Reichert–Meissl, Polenske, and Kirschner processes has revealed, in addition to the necessity for adherence to certain details specified by previous investigators, the distinct possibility of small amounts of sulphuric acid being volatilised and included in the last-mentioned values, unless every

precaution is taken to ensure a perfect fit between the distillation flask and the protecting shield. A specially cut Uralite sheet, together with asbestos paper, has proved suitable for this purpose.

With the adoption of the specified practical precautions, experimental figures have shown the close degree of accuracy obtainable when butter fat of Kirschner value 23·5 has been used in admixture. Similarly, when the Kirschner value of the butter is known and correction can be made for any alteration from 23·5, the accuracy is of a like order. When, however, as usually proves to be the case, the analyst is unaware of the Kirschner value of the incorporated butter, which may, at all events, vary from 19 to 27, he cannot be entitled to state the actual percentage of butter present to a greater degree of accuracy than between the range minus 13 per cent. and plus 24 per cent., both figures being calculated on the reading that would be obtained from the standard graphs drawn up for a butter fat of Kirschner value 23·5.

In conclusion, the authors are desirous of thanking Messrs. Lever Bros., Ltd., for permission to publish this paper.

RESEARCH LABORATORIES,
PORT SUNLIGHT.

DISCUSSION.

Mr. F. W. F. ARNAUD recalled the fact that he has investigated and published a paper on the Kirschner value before it was studied by Richmond, Revis and Bolton. He was of the opinion that it was necessary to obtain a factor for each apparatus, and that this would particularly affect the Polenske value.

Mr. A. ANDERSON said that the paper was a contribution towards elucidating the causes of the differences which frequently occurred in the interpretation of the results of analysis. The authors had shown that the Reichert-Polenske-Kirschner test, when carried out with minute attention to details, must still be regarded as the most reliable method of determining butter fat in admixture with other fats.

Mr. A. MORE was of opinion that in making an estimate of the amount of butter fat present in a margarine or similar fat one must consider the effect on the Kirschner figure of variations due to the kind of butter present. In such cases, it was the practice in the Government Laboratory to report the range of percentages of butter fat which might be present, instead of a definite percentage of butter fat.

With reference to the error caused by the use of a badly fitting asbestos ring, he had in mind two other cases where an error arose from the same source. According to the directions given for use of the distilling apparatus prescribed by the British Engineering Standards Association in the specification for benzol, turpentine, white spirit, the flask must be pressed on to the circular hole of the asbestos. Otherwise, the gases from the burner, passing along the side of the distilling flask, superheated the vapour, and an erroneously high boiling point was recorded. Then in the ordinary Kjeldahl nitrogen process a loss of nitrogen occurred by volatilisation of ammonium sulphate with the sulphuric acid, if any part of the flask above the level of the boiling liquid were directly exposed to the flame of the burner. This might occur either by having too little acid in the flask or by the use of a badly fitting asbestos ring.

Mr. C. A. SEYLER asked if variations in atmospheric pressure had been recorded during the authors' experiments.

Mr. L. V. COCKS replied that the figures obtained by their correction were nearer the actual values than those obtained by the application of any other formula. In confirmation of Mr. More's suggestion, he mentioned that a long-necked Kjeldahl flask was used for distillation in determining the acetyl value, on account of the volatilisation of sulphuric acid. Atmospheric pressures had not been recorded, but consistent readings had been obtained over a wide range of pressures.

Mr. E. NIGHTINGALE issued a warning to the effect that it was essential that absolutely pure silver sulphate should be used.

THE PRESIDENT said that, apart from Mr. Arnaud's paper, the Kirschner value was not in general use when Richmond, Revis and himself gave their attention to it. He had not thoroughly investigated the question of the purity of silver sulphate, but he knew that when he used brands other than Kahlbaums' he did not find them as satisfactory.

The Separation of Lead Tetra-Ethyl from Solution in Petroleum Spirit.

By F. W. TOMS, F.I.C., and C. P. MONEY, B.Sc., A.I.C.

(*Read at the Meeting, May* 2, 1928.)

In view of the remarks of the retiring President of the Society of Public Analysts, Mr. E. Richards Bolton, on the subject of lead tetra-ethyl in motor spirit, the following note, which is the outcome of some work of the Official Analyst of Jersey, Channel Islands, may be of interest.

The Island has considerable powers of local self-government, and, on March 13 last, members of the "States" (or local Parliament) asked the President of the Harbours Committee if "Ethyl petrol" was being introduced into the Island, and if the Committee were taking steps to prevent or control its introduction. The President undertook to consider the matter, and, in view of its chemical nature, directed the Analyst to submit observations.

A brief summary of the position was, therefore, submitted, concluding with the suggestion "that it seems only prudent, in the interests of the health of our people, who have no experience in its peculiarities, to limit its use to the small amount at present imported, as an experiment, and admit no more until the Government decision has been made known in regard to its suitability for ordinary use: this prohibition to be without prejudice to the real question at issue."

The Harbours Committee, after receipt of this report and witnessing certain experiments, adopted the recommendation, and at the next meeting of the States, on March 20, moved that, "until further notice, no more 'Ethyl petrol' should be imported."

Experimental.—In connection with the above report, the following experiments were carried out. They are based on observations made by Professor Edward Frankland and Awbrey Lawrance (see *J. Chem. Soc.*, 1879, **35**, 244), at a time when one of us (F. W. Toms) was a research student at South Kensington, also working on organo-metallic bodies. Frankland and Lawrance concluded:

(2) Prolonged exposure at ordinary temperatures to the following gases produces no chemical change in plumbic tetrethide:—Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen, sulphuretted hydrogen.

(3) Plumbic tetrethide rapidly absorbs sulphurous anhydride, and is transformed into a white solid which is composed of diethyl sulphone (. . . Et_2SO_2) and plumbic ethyl sulphinate (. . . $Pb(SO_2Et)_2$).

It was an obvious inference that passing gaseous sulphur dioxide into "Ethyl petrol" would probably cause decomposition of the lead tetra-ethyl, and, it was hoped, separation of the products would follow. On trying the experiment, a turbidity was produced after 2 hours, and, on standing, the petrol cleared, leaving a whitish deposit on the flask.

Quantitative experiments were therefore put in hand. Five hundred c.c. of "Ethyl petrol" were saturated with sulphur dioxide by passing through it a slow stream (from a siphon) for 4 hours a day on 2 consecutive days; after standing for

36 hours, the clear, pale pink petrol was decanted, leaving the deposited whitish solid adhering to the flask.

The decanted petrol, after a further 4 hours' treatment with sulphur dioxide, and standing for 48 hours, became bleached to a clear pale yellow and deposited a black, tarry residue. This residue, treated as will be described for the whitish solid, proved free from lead.

The whitish deposit first obtained was well moistened with concentrated sulphuric acid (20 c.c.), and 20 c.c. of concentrated nitric acid were added. After standing 4 hours on the steam bath all deposit had been removed from the sides of the flask, and a white precipitate had formed. The whole was washed into a weighed silica dish, three successive quantities of 10 c.c. concentrated nitric acid each being used; the mixture was gently taken to dryness and ignited. Successive treatments with very small quantities of sulphuric and nitric acids, followed by evaporation and ignition, were given, until a pure white residue remained. This residue was weighed, both before and after purification by solution in hot ammonium acetate, as the following table illustrates:

Experiment No.	500 c.c. "Ethyl Petrol" Yielded: Weight of first ignited residue. Grm.	Weight of purified lead sulphate. Grm.	Weight of lead chromate. Grm.	Volume of lead tetra-ethyl (calculated). Per Cent.	Volume of petrol to 1 vol. of lead tetra-ethyl.	Remarks.
(1)	0·6332	—	—	0·0833	1200	Assumed residue was lead sulphate
	—	—	0·6685	0·0826	1211	From ammonium acetate extract of residue.
(2)	—	0·6375	—	0·0839	1192	ditto

The chemicals used throughout were lead-free, giving no reaction for lead in the quantities used in the above experiments.

It may be noted that the molecular weights of lead chromate and lead tetra-ethyl are 323·21 and 323·36, respectively.

Assuming the only figure available to us, 1·62, to be the sp. gr. of lead tetra-ethyl, the following factors give this ingredient by volume:—Lead sulphate, 0·6582; lead chromate, 0·6176.

It will be observed that the agreement between the calculated quantities of lead tetra-ethyl indicates that the white, ignited precipitate is relatively pure lead sulphate. The amount of lead tetra-ethyl indicated is slightly higher than stated by the vendors of the petrol (1 part by volume in 1300 of petrol, maximum concentration).

The examination of other suspected materials by a petrol extraction, followed by the above process, immediately suggests itself.

Summary.—(1) Lead tetra-ethyl may be removed from solution in petroleum spirit by the action of sulphur dioxide.

(2) The insoluble reaction product, when subjected to a process of "wet-combustion," yields relatively pure lead sulphate.

Seasonal Variations in the Composition of the Latex of *Hevea brasiliensis*.

By NORMAN RAE, M.A., F.I.C.

(*Read at the Meeting, February* 1, 1928.)

The information upon the composition of rubber latex which is to be found in the literature upon rubber is very limited. It, therefore, seemed desirable to carry out a series of analyses of the latex of *Hevea brasiliensis*, and also to extend these throughout a whole year, to see if there are any seasonal variations in the composition of either latex or ash. It was thought that such an examination might give some information as to the function of the latex in the tree. The samples were obtained by the kindness of Mr. E. C. de Fonseka, jun., who has a small estate near the laboratory, so that samples could be analysed soon after collection.

The estate is in Colombo, and is being heavily tapped, because the land will shortly be used for building purposes. Tapping was carried out daily, except for 36 wet days, and did not cease during wintering. The estate is three-and-a-half acres in extent, and has 284 trees of an average age of 15 years. The soil is a coconut sand, and is poorer than the usual rubber soil, being low in potash and poor in phosphoric acid and nitrogen. No artificial manure was used, but dead leaves were buried in the soil.

Methods: Electrical Conductivity.—The conductivity of latex rises on keeping, due to the development of acid; therefore the determinations were made, as far as possible, at the same time, after tapping, on each occasion. Tapping commenced in the early morning at about the same time each day, and the samples arrived in the laboratory at 10 o'clock. The conductivity was determined by the Wheatstone bridge method, in a cell in which it gave a resistance of about 600 ohms; and the cell was allowed to stand in a large jar of water for 20 minutes before readings were taken. The temperature coefficient of the resistance was found to be 0·037; the temperatures of the determinations were between 26°–29° C., and the values were corrected by means of the above coefficient to 28° C.

Hydrogen Ion Concentration.—This was determined on the serum obtained by coagulation of the latex with redistilled absolute alcohol. Sufficient alcohol was added to coagulate the latex at 11 o'clock, and by 2 p.m. enough serum had been expelled by the mass of rubber to allow of a determination of the P_H value by Gillespie's method (Analyst, 1920, **45**, 240), with the use of brom-cresol purple. This method was checked with the electrical method, which was found to give similar results. A good deal of trouble was experienced before a suitable train was found, the difficulty being that coagulation occurred at the latex junction. Finally, 0·2 *N* potassium hydroxide was found to give a satisfactory bridge,

and the cell used was mercury, calomel, saturated potassium chloride solution, 0·2 *N* potassium hydroxide, latex, hydrogen gas, platinum. A rocking gas electrode was used. The P_H falls with time; for instance, a sample had the value 6·3 at 11 a.m., and 6·1 at 3 p.m. The values at the time of tapping were, therefore, about 0·3 higher, giving an average value of 6·5; *i.e.* the serum was practically neutral to litmus, and alkaline to methyl orange and phenolphthalein.

MOISTURE.—This was determined by heating 10 grms. of latex in a platinum dish in the electric oven for three days at 80° C.

ASH.—The residue from the moisture determination was heated at 500° C. in an electric furnace, then cooled in a desiccator and weighed as rapidly as possible, since the ash is very deliquescent.

PROTEIN.—This was determined by the Kjeldahl method on 5 grms. of latex. The factor 6·25 was used to convert nitrogen to protein. This factor is considered to be too high, but, in the absence of knowledge as to the correct value, it is used to facilitate comparison with the results of other experimenters.

RUBBER.—Two grms. of latex were added to benzene, and the whole was made up to 200 c.c. After being shaken occasionally for 3 days, the solution was allowed to stand overnight, 50 c.c. were pipetted off, evaporated in a platinum basin on the water bath, and the residue dried in the oven at 80° C. and weighed.

RESIN.—Ten grms. of latex were weighed out on to filter paper and dried at 80° C. The paper was then cut up, and extracted with acetone in a Soxhlet extractor on the water-bath for 24 hours.

POTASH AND PHOSPHORIC ACID IN ASH.—The rubber from the P_H determination, together with the serum used, was slowly carbonised over a small flame. The product was then ashed in an electric furnace at 600° C. overnight, and a good white ash was obtained. Phosphoric acid in the ash was determined by Woy's molybdate method, and potassium by the cobaltinitrite permanganate method.

RESULTS.—In addition to the results given in Table I, the combined residue of all the latex ashes was analysed, and also the ash from leaves, seeds and wood.

The leaves and wood give an ash containing considerable quantities of carbonate of lime and iron, whilst the seeds give an ash containing very little carbonate or iron.

The results were:

	Leaf. Per Cent.	Seed. Per Cent.	Wood. Per Cent.
Potassium oxide	11·7	29·7	16·2
Phosphoric anhydride ..	15·3	27·9	11·1

	Latex ash. Per Cent.		Latex ash. Per Cent.
Silica	2·4	Potassium oxide	44·3
Alumina	0·3	Sodium oxide (by diff.) ..	9·1
Ferric oxide ..	nil	Sulphuric acid (SO_3) ..	2·8
Lime	2·8	Chlorine	0·3
Magnesia ..	5·6	Phosphoric anhydride ..	32·4

		Nut (3 in one shell).	
	Shell.	Seed coat.	Kernel.
Average weight, grms. ..	15·54	1·47	1·84
	Per Cent.	Per Cent.	Per Cent.
Ash	0·28	2·13	2·14
Protein	1·37	2·49	14·31
Moisture	1·46	12·55	31·17

It will be seen that the ash of latex is very rich in both potash and phosphoric acid.

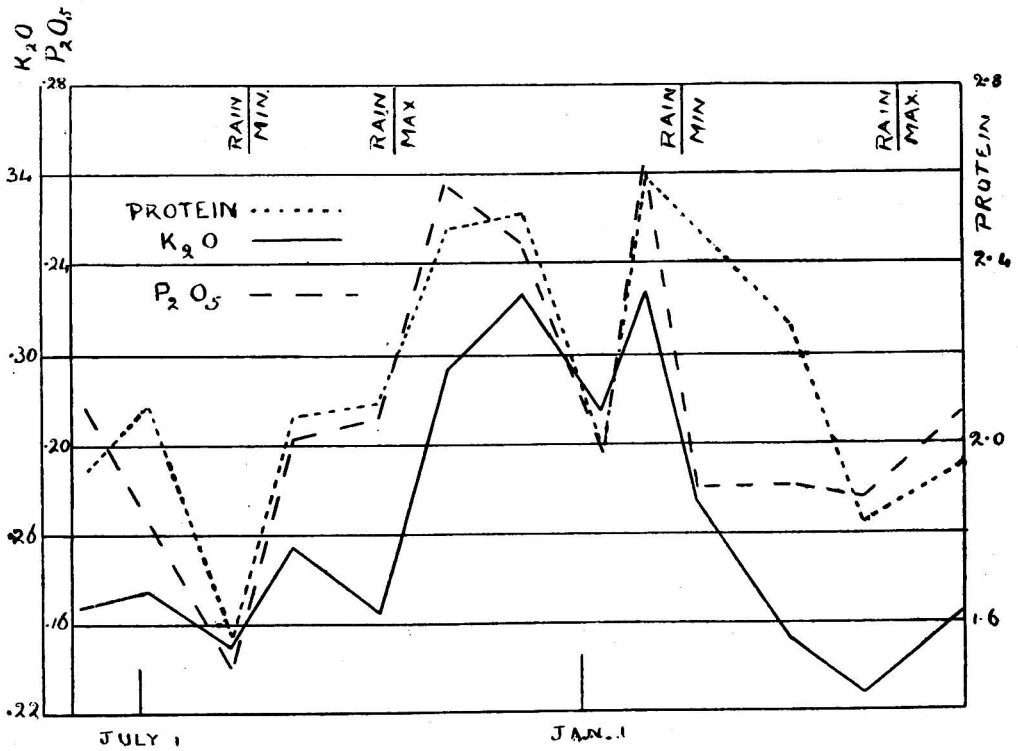
The general results are shown in Table I. It will be noticed that the totals are always two or three per cent. high; the error can only be due to the rubber or the water, or both. It is possible that the benzene extracts more from the latex than the rubber, and also that the prolonged heating at 80° C., necessary to drive off all the water, at the same time causes, to some extent, decomposition of the rubber. If latex is left in the oven a couple of weeks it becomes soft and very sticky; there is then no doubt that decomposition has commenced, and I am inclined to think this is the main cause of the error.

Date.	P_H.	Conductivity at 28° C. $\times 10^{-6}$.	Rubber. Per Cent.	Resin. Per Cent.	Protein. Per Cent.	Ash. Per Cent.	Water. Per Cent.	Total. Per Cent.	K_2O. Per Cent.	P_2O_5. Per Cent.	Inches of rain in last 28 days.
1926.											
July 5	6·7	2680	40·54	1·85	2·09	0·60	58·60	103·71	0·246	0·177	14·3
Aug. 6	6·3	2800	39·92	1·34	1·57	0·52	59·13	102·48	0·236	0·150	8·9
Sept. 2	6·3	3240	40·54	1·31	2·06	0·60	58·91	103·42	0·257	0·201	4·8
Oct. 8	6·6	2660	39·14	1·72	2·09	0·58	59·18	102·71	0·242	0·206	10·4
Nov. 3	5·9	3480	34·57	1·35	2·44	0·69	62·62	101·67	0·296	0·258	11·6
Dec. 6	5·8	3490	36·03	2·00	2·47	0·75	61·40	102·65	0·313	0·245	10·6
1927.											
Jan. 7	5·7	3310	40·84	1·21	1·97	0·63	57·51	102·16	0·206	0·197	7·1
Jan. 27	5·8	3910	34·95	2·10	2·59	0·81	62·62	103·08	0·314	0·262	6·3
Feb. 18	6·3	2960	39·31	1·64	2·44	0·58	59·07	103·04	0·267	0·190	3·0
Mar. 30	6·2	2730	39·17	1·90	2·26	0·54	59·33	103·20	0·237	0·190	5·9
April 28	6·2	3140	29·40	1·56	1·82	0·51	68·57	101·86	0·225	0·188	7·2
June 9	6·3	2720	35·20	1·63	1·95	0·58	62·89	102·05	0·243	0·207	18·5
Average	6·2	3090	37·30	1·63	2·15	0·62	60·82	102·67	0·257	0·206	

Discussion.—In considering the results in relation to rainfall a diagram was made in which the ordinates represented inches of rain per 28 days. Maxima of rainfall occurred in the middle of October and May, and minima in the middle of August and February. It was found that the variations in resin, water, rubber, and P_H value show no relations among themselves or with the rainfall.

As was to be expected, a relationship between the conductivity and the ash of the latex was established, and it was also found that there is a general correspondence between the proteins present in latex and the ash, and, therefore, the mineral salts. This is very well brought out in the diagram, where protein, potash and phosphoric acid are all plotted. Here we have a fairly close correspondence

between the three substances which are absorbed through the roots of the plant for the purposes of growth, and which are, therefore, the substances required in manures; namely, nitrogen, phosphoric acid and potash. The relation shown between these three is obviously of considerable significance, as is also the high proportion of potash and phosphoric acid in the ash. When the form of the curves is examined, the three substances are seen to be at a minimum in August, when seed fall occurs; they increase in amount till February, then there is a large decrease until May, followed by a slight increase to July, and a drop to August.



The main feature is the large increase from August to February, and the large drop which follows. The January figures are all low, and I am unable to account for this unless it is in some way connected with the tapping over the previous days; I can only regard it as an abnormal sample.

The minimum occurs at the time of seed fall, and during the next six months the amount of these substances increases until we reach the period of leaf fall, and the consequent growth of new leaves, when it undergoes a large fall. This is followed by a partial recovery and a further fall, when the seeds are maturing. This seems to suggest a connection between the two, and that the latex may serve as a means of storing these substances until the periods of active growth, when they are used up. The latex vessels are long single cells between the cambium and the

bark, and it may be that they are useful, not so much for supplying food for leaf growth as for bark growth, thus relieving the transpiration current of part of its normal work at a time of stress.

The above is an attractive view, but another possibility may be suggested. The latex in a tapped tree has to be renewed continually in the plant; but at the time of leaf production the energies of the plant are all directed towards this end; there is, therefore, less food available for replacing the latex which has been removed. I do not think this is so, and in this connection the work of L. E. Campbell (*Bull. 22, Dept. of Agriculture,* Ceylon) is noteworthy. He describes experiments on the storage of starch in the bark and in the wood of *Hevea* trees. He found that in the bark the starch reaches a maximum when leaf fall occurs, and that it decreases rapidly to zero during the short period (about two weeks) between the appearance of the new leaves and their full growth. Thereafter it increases in amount till June, drops to a low value in September, and then rises to a high value again, which is maintained till February. There is thus very considerable similarity in the variation in starch in the bark, and that in protein, potash and phosphoric acid in the latex. Campbell's trees were untapped. He concludes that the fall in April is due to the starch being used up in leaf growth, but he does not comment on the low values found in September.

SUMMARY.—1. Monthly analyses of the latex of *Hevea brasiliensis* and its ash have been made throughout a year.

2. Nitrogen, potash and phosphoric acid are found to rise to a maximum in February, to fall until May, increase somewhat till July, and then to fall to August.

3. Leaf fall and renewal of leaves coincides with the fall in March, and maturing of seeds with that in July.

4. It is suggested that the latex is a food reserve to be used up when leaf growth and seed growth are most actively proceeding.

CEYLON UNIVERSITY COLLEGE.

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.

TESTS FOR RECONSTITUTED CREAM.

INCREASING quantities of reconstituted cream are being made, and it will be necessary for the analyst to distinguish between ordinary or fresh cream and the reconstituted article. I have experimented with reconstituted cream of excellent quality. This article is indistinguishable from ordinary cream, either directly to the taste or when used in tea or coffee, etc. The article in question is made

by combining dried separated milk, saltless butter and water in correct proportions, giving an emulsion with about 50 per cent. of butter fat.

If 5 c.c. or 5 grms. of the cream are shaken with a mixture of equal parts of benzene and methylated spirit (60 O.P.), and the mixture is then centrifuged, the reconstituted cream will throw up its butter fat as an amber upper layer, whilst the fresh cream will remain as an emulsion with no appreciable separation of the fat layer. After strong centrifuging the reconstituted mixture shows three distinct layers, whilst the fresh cream mixture shows only two layers, *viz.* the aqueous lower layer and an upper opaque stratum. The results are the same, even when the cream has become sour.

The reconstituted cream above described had been submitted to a sterilising process at 145 F. for several minutes, and, as was to be expected, it gave no reductase action with methylene blue, whilst the "fresh" cream of the same date gave an almost instantaneous reduction. When larger amounts of the blue were used and the mixtures were heated at 82° F. the difference was very marked.

F. W. RICHARDSON.

CITY AND COUNTY ANALYST'S OFFICE,
BRADFORD.

GLYCERIN IN CREAM.

THE suggestion that glycerin should be used as a cream preservative has been made recently, and enquiries have been set on foot as to the position that would be adopted by Public Analysts and others in relation to such a practice.

Glycerin is, of course, included among those substances, more or less harmless or naturally-occurring, which need not be regarded as preservatives, for the purposes of the Preservatives Regulations, and their presence in an article of food does not constitute an offence. On the other hand, if the addition of glycerin to cream increased its viscosity, it would then come within the definition of a thickening agent. In any case, one would imagine that the addition of glycerin without notice would be regarded as being to the prejudice of the purchaser.

DETECTION.—The presence of glycerin in cream is readily detected during and immediately after the determination of the total solids. One or two grms. of cream in a flat-bottomed dish are heated (well spread out) on the water-bath for 20 minutes, and then in the steam oven for half-an-hour. On removing the dish from the oven and observing carefully, fumes may readily be seen rising from the cream solids if as little as 1 per cent. of glycerin is present. After cooling and weighing; an additional 1 hour's heating in the oven is given. Genuine cream will show a gain in weight, which varied, in my experience, from 1 to 6 mgrms.; a glycerinated cream will show a loss in weight. Further heating in the oven will cause either a slight increase or no change in weight in the case of pure cream, but in the presence of glycerin loss in weight occurs for several hours. The difference between the pure and glycerinated article in this respect is very marked.

The solids of a cream, after about two hours' heating, begin to brown slightly, but when as little as 1 per cent. of glycerin is present the solids assume a very much darker colour.

Observation of these three features during the solids determination on a cream, namely, (1) losing weight, (2) fuming, (3) browning, indicates fairly definitely the presence of glycerin, but in all cases its presence should be confirmed.

PRESERVATIVE ACTION OF GLYCERIN ON CREAM.—The amount of glycerin which it has been proposed to incorporate in cream for preserving purposes is rather less than 1 per cent. An experiment was, therefore, made to see to what extent glycerin in cream had any preservative power.

Six portions of mixed cream, containing, respectively, 0, 1, 2, 3, 4, and 5 per cent. of glycerin, were kept in open beakers under a bell-jar for ten days, and the acidity of each sample determined at intervals. The presence of glycerin apparently had no effect on the rate of souring; the glycerinated samples increased in acidity at exactly the same rate as the original cream. So far as could be judged by tasting, glycerin had no preserving action on the cream under these particular conditions.

My thanks are due to the Birmingham City Analyst for permission to publish this note.

A. F. LERRIGO.

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.

COD-LIVER OIL TABLETS DEFICIENT IN VITAMINS.

ON April 4, a firm of manufacturing druggists was summoned at Salford for the sale of cod-liver oil tablets not of the nature, substance and quality demanded.

Mr. H. H. Tomson, for the Salford Corporation, said that, although there was no legal standard for cod-liver oil tablets, yet it had been laid down that the Court must fix its own standard on the evidence submitted by the prosecution, unless that evidence was contradicted by other facts.

According to the certificate of the City Analyst (Mr. H. H. Bagnall) the sample contained, in addition to other ingredients, 3·2 per cent. of oil agreeing in characteristics with an alcoholic extract of cod-liver oil. When examined by the colour test the oil extract was found to be lacking in vitamin *A*. The certificate went on to state that "These are not cod-liver oil tablets, since the oily matter contained in them lacked the essential vitamin *A*, which was one of the most valuable constituents of cod-liver oil, and gave it a large part of its therapeutic value. Apart from its lack of vitamin, the value of the contained oil was negligible, inasmuch as about 160 tablets would have to be taken to obtain the minimum dose of cod-liver oil." The tablets were also analysed by Mr. G. D. Elsdon, the Lancashire County Analyst, and his conclusions were similar. The prosecution, however, had not been undertaken on the chemical evidence alone. Part of Mr. Bagnall's sample was sent to the laboratories of the British Pharmaceutical Society, and biological tests had been made there with rats, which showed the absence of both vitamins *A* and *D*.

Mr. J. Whitehead, K.C., for the defence, interposed, and said that he was not in a position to discuss what had taken place in the London Laboratories, and was prepared to meet evidence concerning vitamin *A* only.

The Stipendiary: "Are these cod-liver oil tablets, or are they not?" Mr. Whitehead replied that they had not been acquainted with the results of the animal tests, and that he was therefore prejudiced in preparing a defence.

Mr. Tomson submitted that, having served the Analyst's certificate, they were not precluded from calling any other evidence they wished. After further argument it was decided to hear the evidence.

After evidence had been given by Mr. Bagnall and by Mr. Elsdon with respect to the analysis, Dr. J. H. Burn, the Director of the Pharmacological Laboratories of the Pharmaceutical Society, said that there were certain guides with regard to the presence of cod-liver oil in a preparation. One guide was the U.S. Pharmacopœia, which stipulated the presence of vitamin *A*, and another was that it should possess the power of curing rickets. In his opinion these tablets, as a substitute for cod-liver oil, were worthless.

Dr. Katherine Coward said that she had made the actual tests on the tablets and explained the technique used. Rats, weighing 40 to 50 grms., were given a diet, previous to the test, free from vitamin *A*. As the tablets were said to contain a concentrated extract of cod-liver oil, rich in vitamins, and as the sugar coating constituted about one half the weight of each tablet, it was decided to use a dose of 0·01 grm. of the ground-up tablet. As a result of the test, the rats used all died within 14 days, whilst others, which received a daily dose of 0·002 grm. of cod-liver oil, ceased to lose weight and resumed normal growth.

A further test to determine whether the tablets would cure rickets in rats gave negative results, whereas a similar dose of cod-liver oil cured rickets in other rats of the same batch.

Mr. Whitehead submitted that, as there was no definite standard for cod-liver oil laid down in the British Pharmacopœia, the prosecution had failed to prove their case. Since his clients were not concerned with the manufacture of the tablets, beyond making up the ingredients supplied to them by the firm whose name was given to the tablets, they were not prepared with any evidence with regard to animal tests. The article was, in fact, a proprietary one, and therefore was excluded from the operation of the Act.

The Stipendiary Magistrate (Mr. P. W. Aitken) imposed a fine of £30 with 75 guineas costs. Leave was given to the defendants to appeal.

SALE OF PEACH OR APRICOT KERNEL OIL AS ALMOND OIL.

On April 20th, a druggist was summoned at Birkenhead Police Court for selling almond oil not of the nature, substance and quality demanded.

Mr. H. E. Davies, Public Analyst, said that he had applied a colour test which showed that the sample was not almond oil, but contained a large proportion of oil derived from the kernels of peach or apricot stones. He judged by the intensity of the colour reaction that what was sold was either all kernel oil from one of these sources, or mainly so.

The solicitor for the defence objected to the form of the Analyst's certificate, on the ground that it did not, as required by the Food and Drugs Act, state the percentages of foreign ingredients, but the Bench ruled that the certificate was admissible.

For the defence it was urged that there were two kinds of almond oil, *viz.* almond oil *persic.* and sweet almond oil. Defendant's sale for the former was considerable, whilst he sold hardly any sweet almond oil. When asked for "almond oil," he sold almond oil *persic.*, unless specially asked for sweet almond oil. The customer had been charged the cheaper price for the sample.

The defendant was fined 8s. 6d. and the analyst's fee.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION. Special Report No. 31.

THE CHANGES PRODUCED IN MEAT EXTRACTS BY THE BACTERIUM *STAPHYLOCOCCUS AUREUS*.*

THE Report deals with the application of the alcohol titration methods to the investigation of changes produced in meat extract media by bacteria, especially *Staphylococcus aureus*. The cultures were made from simple extracts of fresh bullock's heart, and, to prepare the alcohol extracts, a portion of each culture was mixed with 9 vols. of 97 per cent. (by vol.) alcohol of known acidity, so that the mixture contained 87–88 per cent. of alcohol, the clear liquor being the "alcohol extract" and the precipitate the "alcohol precipitate." An aliquot portion of the liquor is immediately titrated to phenolphthalein with carbonate-free 0·01 *N* sodium hydroxide solution standardised to phenolphthalein. The differentiation of the "total alcohol value" of "alcohol extracts" into class values involves the elimination and determination of volatile bases, and in the residual liquor the determination of "regenerated alkali" equivalent to the sum of the values for non-volatile amines and the "internal salt" carboxyls of amino acids. These two latter values are then determined in the neutral solution resulting from the "regenerated alkali" determination, and by taking the difference between the "regenerated alkali" value and the Sörensen value of the neutralised residual liquor. Finally, the "net acidity" is found, which affords a measure of the free acid value of the constituents of the "alcohol extract," if they were in aqueous instead of alcoholic solution.

The elimination and determination of the HCO_3 radicle in "alcohol extracts" depend on the principle that, compared with water, alcohol or strongly alcoholic solutions exhibit very feeble retentive powers for carbon dioxide. This is removed at room temperature, and, as only a very small amount of free hydrochloric acid is present and the solution is alcoholic, the other constituents are not exposed to risk of change. The "alcohol precipitate" is filtered off, washed with 88 per cent. alcohol, made up with water and titrated to phenolphthalein. The alcohol titration values of "alcohol precipitates" may also be differentiated into class values. Many substances insoluble in 87–88 per cent. alcohol are not precipitated if glycerin is added to the aqueous solution before the alcohol, and are held in solution so that their alcohol titration values can be determined. The constituents of the "alcohol precipitates" from sterilised meat extracts, chiefly phosphates, complex protein derivatives and peptids, respond thus. Analytical figures are checked by "balance sheets."

As a result of the many recorded experiments it appears that in the late stages of a prolonged incubation at room temperature the organisms in concentrated media attack volatile acid radicles in preference to amino acids and non-volatile amines, whilst at 37° C., after non-volatile acid radicles have disappeared, the bacteria utilise both amino acids and non-volatile amines, and destroy volatile acid radicles at a much slower rate. In concentrated media internal changes occurring whilst the organisms are attaining their first peak seem to be independent of air supply, whilst consequent changes seem to be oxidative in character,

* By F. W. Foreman and G. S. Graham Smith. Obtainable at Adastral House, Kingsway, W.C.2. Price 2s. net.

so that by controlling the air supply it might be possible to increase the yield of some desired volatile acid which the organism produces. A separate report (Foreman and Graham Smith, *infra*) deals with the importance of the different classes of constituents in endowing the cultures with capacity to resist changes of P_H within the region of P_H covering the field of ordinary physiological study. In meat extracts the phosphates and creatinine are chiefly responsible for resistance to change of $[H^+]$ on adding acids. The methods given enable a satisfactory determination of acidity of a culture to be made in the presence of pigment, etc., and an accurate figure can be obtained for the total acid radicles, the acid groups in "internal salts" of amino acids, etc. (Foreman, 1928, I). Thus, acid radicles combined in salts of tertiary amines and in salts or "internal salts" of bases of the secondary amine type, which in formol titrations respond negatively and only partially, respectively, are included quantitatively. Consequently, in meat extracts the results embrace the whole of the acid radicle fluctuations, apart from the exceptions mentioned, the values with which are probably negligible, and render possible the indirect determination of classes of constituents, such as the total non-volatile acid radicles, for which no reliable method of determination, direct or indirect, existed previously. The Sörensen-formol method does not give a satisfactory total acid radicle figure, principally because the acid radicles combined with secondary amines or imino groups generally are titrated only partially, and the acid radicles in salts of tertiary amines not at all. Comparisons of the formol and alcohol titration values supply valuable information.

D. G. H.

Special Report No. 32.

THE CONTROL OF REACTION IN CULTURES AND ENZYMIC DIGESTS.*

THE relations between the fluctuations in hydrogen ion concentration and titratable acidity of cultures during incubation observed in experiments described in Special Report No. 31, were further examined, and in one particular experiment the P_H of culture VII was 5·64 at the commencement of incubation; from 0 to 164 hours the total amplitude of P_H variation was 0·31, but from the 164th to the 1025th hour it fell by 1·63 to 7·11. In culture VIII it fell still further, probably to about 7·6. Creatinine and inorganic phosphates were found to be largely responsible for the methyl orange value of the culture, so that with a P_H of about 7·6 at the 344th day of experiment VIII the sum of the methyl orange values if titrated from the P_H, calculated from their ascertained content, was equivalent to about 87 per cent. of the methyl orange value of the whole culture. Constituents other than creatinine and phosphates collectively accounted for only 10–15 per cent. of the methyl orange value.

The influence of amino acids is insignificant, that of ordinary salts of organic acids in volatile bases and non-volatile amines present in large amounts only a fraction of the extent expected, and aqueous solutions of creatine and betaine present in the culture in very small quantities, required 3–4 per cent. of one equivalent of hydrochloric acid to methyl orange, whilst colloidal matter exercises some effect. The P_H zones in which the two important buffering constituents are most effective were then distinguished. The flat portion of the titration curve of

* By F. W. Foreman and G. S. Graham Smith. Obtainable at Adastral House, Kingsway, W.C.2. Price 9d. net.

the phosphates extends from about P_H 7·2 to 6·3, and that of creatinine from about 5 to 4·5, and, calculated in terms of their titration values with hydrochloric acid from about P_H 9 to 4, the quantities of inorganic phosphates and creatinine (including any substance present with similar titration properties) in the concentrated heart extract were in the proportion of about 1·7 to 3·0, other constituents collectively playing a very minor part in the buffering of added acid. No definite conclusions resulted from attempts to associate the behaviour of the phosphates and creatinine with the P_H and acidity values of the culture as incubation proceeded.

Curves representing ratios of percentage increase in $[H^+]$ to percentage increase in acidic H concentration for successive increments of acid involved in Sörensen's phosphate data, and the changes in extent to which the free acid was dissociated at the various stages, were closely similar in contour, of low gradient at first, until, at later stages the lines became almost vertical. The term "depressor effect" is used in reference to resistance to change of $[H^+]$ as seen in the "per cent. dissociated" curves, and the higher the dissociation constant of the acid of the depressor salt the higher position on the $[H^+]$ scale will its "optimum point" occupy, and the higher the level of the range of $[H^+]$ over which the salt exercises its depressor effects.

It is concluded that there is sufficient justification for the view that the effects of salts upon the activities of enzymes and bacteria in media should be considered from the standpoint of how these affect the absolute $[H^+]$ and $[OH^+]$ as well as the P_H value. In the construction of artificial media these two standpoints involve two different ways of employing salts.

D. G. H.

THE NATIONAL PHYSICAL LABORATORY.

REPORT FOR THE YEAR 1927.*

THE present volume includes the report of the Executive Committee, a statement of work for 1928–29, and the detailed reports of the Physics, Electricity, Metrology, Engineering, Aerodynamics, and Metallurgy Depts., and also of the William Froude National Tank.

PHYSICS DEPT.: *Industrial X-ray Crystal Analysis.*—The new section has begun work, and has examined 6 per cent. tungsten steels containing 0·7 per cent. of carbon, with special reference to their use as permanent magnets. Water-quenching of this steel from 850° C. causes the appearance in the X-ray photographs of a group of lines other than the α-iron lines, whilst continued heat treatment at 950° C. produces a marked improvement in their definition, but results in a drop in value of the coercive force of the steel. A short heating at 1250° C. and air cooling, causes a disappearance of the lines, and in steel so treated and water-quenched at 850° C., the lines reappear, and the spoiled steel can once more be made of good magnetic quality.

Spectrophotometry. Ultra-Violet Absorption.—Improvements in the technique of 1926 have been effected. Several methods of measuring photo-electric currents have been used successively or in conjunction, but one method which is the most sensitive is in general use over the entire range of wave length employed. New sodium photo-electric cells with quartz windows are used, covering the ultra-violet spectrum as far as a wave length of 0·23μ. An investigation of the transmission of a number of standard substances for comparison of results by different

* Obtainable at Adastral House, Kingsway, W.C.2. Price 7s. 6d. net.

methods has been begun. Colour measurements of 3-colour mixture curves of the normal eye have been proceeded with, and a complete set of values obtained for each of seven observers, and a method of correcting the observations of any observer to agree with the mean of a number is being evolved. Brightness and visual fatigue need not be considered in colour matching with standard fields. The form now adopted for the numerical statement of results of colour measurement is as follows :—

$$Q = \alpha R + \alpha' G + \alpha'' B$$
$$S = p \text{ per cent.}$$

In this statement $\alpha + \alpha' + \alpha'' = 1$, so that the Q formula denotes simply the *quality* of the colour, irrespective of its brightness, and the S term, which determines the shade, refers to the degree of brightness, evaluated on a luminosity basis, irrespective of the quality of the colour. In the case of opaque material, S is expressed as a percentage of the brightness of a magnesium oxide surface under the same illumination. Any statement of colour presupposes that it is taken under laboratory standard conditions.

METROLOGY DEPT.: *Glass Volumetric Apparatus and Hydrometers.*—In testing graduated flasks for errors the gravimetric method (always employed) was compared with the volumetric for 100 ml. flasks, and the volumetric tests always gave a lower flask capacity than the gravimetric. This was found to be due to the difference in curvature of the meniscus. Different surface tensions are present according to whether any contamination is concentrated in the small water surface in the neck of the flask, or removed. The discrepancy is considerably less than the tolerances ($\pm$0·06 ml. for Class A, 100 ml. flask, and $\pm$0·10 ml. for Class B); but, allowing the average discrepancy, the volumetric test would not be adequate for Class A with certificate. The Committee on Dairying have suggested the collection of information, with a view to the standardisation of glassware for testing milk and milk products throughout the Empire. The total number of glass volumetric apparatus tested during the year was 3367, compared with 4667 the previous year.

Hydrometers.—It was found that, if due allowance is made for surface tension when testing hydrometers, a high degree of accuracy may be obtained, but quite considerable inconsistencies may otherwise arise. The number of hydrometers tested during the year was 679, compared with 801 the previous year.*

D. G. H.

* *Erratum* :—In the Abstract of the Report for 1926 (ANALYST, 1927, **52**, 413) the year was given as 1927 instead of 1926.

Ministry of Health.

MEMORANDUM ON THE FUMIGATION OF SHIPS WITH HYDROGEN CYANIDE.*

THE nature of hydrogen cyanide is explained, and stress is laid upon the point that it is a fallacy to imagine that because the gas is lighter than air it can be induced to escape upwards merely by opening portholes or hatches of ships. The whole atmosphere must be changed by applying the known principles of ventilation. It is highly dangerous to rely on the sense of smell for detecting the presence of the gas.

* H.M. Stationery Office, 1928. Price 1d. net.

In Sec. II the methods of generating the gas for fumigation purposes are described. Sec. III deals with the general precautions that must be taken, the most essential of which is that fumigations must only be carried out by trained persons. Special precautions with regard to handling, storage, warning notices, and naked lights are given.

Section IV deals with the routine to be followed, and Sec. V with opening up and ventilation. To insure the complete absence of hydrogen cyanide, the chemical test of Sieverts and Helmsdorf is occasionally used. This consists in exposing strips of filter paper, moistened with a freshly-prepared solution of copper benzidine acetate, to the atmosphere to be tested. The paper will be coloured blue in a few seconds if as much as 1 part of hydrogen cyanide in 10,000 is present.

Section VI deals with the disposal of residues, etc.; Sec. VII with gas masks (which should be worn, or at least be available for immediate use); Sec. VIII with the symptoms of cyanide poisoning; and Sec. IX with rescues and the resuscitation of persons overcome by the gas. The Memorandum concludes with directions (with diagrams) as to the application of artificial respiration.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Chlorine in Bleached Flour. A. Seidenberg. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 132–135.)—The sample (20 grms.) is well mixed with 60 c.c. of 70 per cent. ethyl alcohol, and heated gently on the water-bath, 60 c.c. of 95 per cent. alcohol are added, and the mixture well shaken, cooled, and again shaken with 75 c.c. of ethyl ether and 150 c.c. of petroleum spirit. The liquid mixture is then decanted into a separating funnel, the residual flour washed with two 40 c.c. portions of petroleum spirit, and the combined solvents washed with 30 c.c. and 10 c.c. of water, separated, and evaporated with 10 c.c. of an alcoholic solution of sodium hydroxide. (If 40 grms. of metallic sodium are allowed to react with 1000 grms. of 95 per cent. alcohol, this last reagent is obtained almost chloride-free.) The residue is charred at a low heat, boiled with a little water, and 5 c.c. of nitric acid (1 : 3), filtered into a flask calibrated at 100 c.c. and 110 c.c., and the residue again boiled with water, and 25 c.c. of 0·005 *N* silver nitrate added to the total filtrate in the flask. This is then placed in boiling water for 5 minutes, cooled, the contents made up to 110 c.c., mixed, filtered, and 100 c.c. of the clear filtrate pipetted out. This is titrated with 0·005 *N* potassium thiocyanate solution in the presence of a cold saturated solution of ferric ammonium sulphate (the brown colour of which has been dispersed by nitric acid), till a permanent red colour is obtained. The blank on the reagents is deducted, and the results calculated on the " dry flour " basis. The method is superior to those previously suggested, in that it ensures complete extraction of the flour, and

exclusion of any natural chlorine from the ash. Volhard's method of titration is preferable to Mohr's, since it is conducted in acid, and not neutral, solution, and the conditions are more accurately reproducible in the determination of the blank. The results were concordant to within 7 parts per million, and enabled bleached and unbleached flours to be distinguished easily. In the latter case they were within the experimental error, and in the former the amounts of chlorine found for a particular flour were consistently less than those actually used. (*Cf.* ANALYST, 1925, **51**, 150.) J. G.

Constituents of the Fatty Acids of Soya-bean Oil. K. Hashi. (*J. Soc. Chem. Ind., Japan*, 1927, **30**, 221B.)—Employing the lead salt and alcohol method of Twitchell, the author found 10·6 per cent. of solid and 85·4 per cent. of liquid fatty acids. The solid fatty acids consist of large amounts of palmitic and stearic acids, and (probably) small amounts of arachidic acid. Calculating from the proportion of bromine in the ether-soluble and ether-insoluble liquid fatty acid bromides, he concludes that the soya bean fatty acids had the following composition :—Linolenic acid, 2·9 ; linolic, 51·5 ; oleic, 35·6 ; and solid fatty acids, 11·1 per cent. R. F. I.

Isolation of Dipalmito-olein from Soya-bean Oil. K. Hashi. (*J. Soc. Chem. Ind., Japan*, 1927, **30**, 222B.)—Soya-bean oil was dissolved in 3 volumes of acetone and cooled to – 10° C. After recrystallisation a compound was obtained with saponification value 202·5 and an iodine value 43·2. The lead salt and alcohol method showed the proportion of liquid to solid fatty acids to be 1 : 2, the latter having a melting-point of 61° C. (the m.pt. of palmitic acid), and the former an iodine value of 107. After oxidation of the liquid fatty acids by a modification of Hazura's method, the melting point of the ether-soluble hydroxy-acids was 127° C., and the melting point of the ether-insoluble, water-insoluble hydroxy-acids was 130° C. The conclusion drawn was that the liquid fatty acids were mostly oleic acid. The acetone precipitate originally obtained, on further purification with acetone, melted at 27–28° C., and had an iodine value of 35·3, which is close to the theoretical value for dipalmito-olein. R. F. I.

Determination of Shell in Cocoa Products. E. Alpers. (*Z. Unters. Lebensm.*, 1927, **54**, 462–466.)—The method of Griebel and Sonntag (*ibid.*, 1926, **51**, 196) has been modified and tested for cocoa mixtures of known compositions. The sample is boiled with 200 c.c. of water and 5 c.c. of 25 per cent. hydrochloric acid for 10 minutes, filtered, and the residue washed with hot water till neutral, and then centrifuged with hot water. Dilute sodium hypochlorite solution (*eau de Javelle*) is then added, and the number of stone cells counted under the microscope. The values obtained depend on the degree of the grinding process, which may destroy or deform the cells. Determination were made for a number of samples of various origins, and the highest value found for Accra cocoa, the annual production of which is greater than that of any other brand.

The mean value of 9337 per mgrm. of dry fat-free substance was found, and it is suggested that this should be called 10,000 and used as a standard for such measurements. J. G.

Determination of Crystallised Digitalin. E. Perrot and P. Bourget. (*Comptes rend.*, 1928, **186**, 1021–1024.)—The crystallised digitalin used in France is sensibly identical with the products named digitoxin by Schmiedeberg and by Kiliani, but Cloetta's digitoxin is a special glucoside occurring in commercial crystallised digitalins in proportions varying from 20 to 75 per cent. To determine the crystallised digitalin in digitalis, 20 grms. of a homogeneous sample are powdered and passed completely through a number 30 sieve, 25 grms. of the powder being extracted for an hour with 200 c.c. of boiling 75 per cent. alcohol in a reflux apparatus. The liquid is filtered while hot and the extraction of the powdered residue repeated with successive quantities of the alcohol until no coloration of the solvent occurs, four extractions usually being sufficient. The total extract (about 800 c.c.) is treated with 20 c.c. of basic lead acetate (Codex) and the alcohol distilled off, the residue being dried on a large clock-glass, first on a steam-bath and then in a steam-oven. The brownish-green residue is powdered and extracted with cold chloroform, best in presence of lead shot, the extraction being continued for 24 hours, with frequent shaking. The chloroform solution is filtered through dry sodium carbonate and then freed from chloroform by distillation from a small flask. The residue is heated for an hour on a steam-bath with 5 c.c. of pinene, which dissolves the chlorophyll and oily and waxy matters, but not the digitalin. The cold liquid is mixed with an equal volume of ether, the green liquid being decanted, after 12 hours, from a brownish precipitate adhering to the wall of the flask. Any loose precipitate is separated by centrifuging, and is mixed with a small quantity of ether and returned to the flask, which is washed with ether until this is no longer coloured, each amount of the solvent being centrifuged. The flask and the centrifuge tube are dried at 100° C. until free from ether, the residues being treated with successive quantities of chloroform until no further solution occurs. The total chloroform extract, mixed with 0·1 grm. of " carboraffin," usually becomes colourless after about six hours, and is then filtered through powdered fused sodium carbonate and distilled until 1 or 1·5 c.c. remains. This is introduced into a centrifuge tube tared exactly in relation to a slightly heavier tube, 10 drops of ether and 12 c.c. of petroleum spirit (b.pt. below 60° C.) being added and the tube stoppered. After 4 hours the tube is centrifuged, the digitalin collecting into a pale yellow plug which melts at 240–247° C., and gives all the reactions of crystallised digitalin. T. H. P.

Halibut Liver Oil. *Erratum.*—In the abstract on halibut oil (p. 291) the iodine value, 16, refers to the solid, not to the liquid fatty acids.

Biochemical.

Determination of Amino Acid Nitrogen in Animal Tissues. J. M. Luck. (*J. Biol. Chem.*, 1928, **77**, 1–12.)—The methods of Folin and Denis (*J. Biol. Chem.*, 1912, **11**, 527) and of Van Slyke (*J. Biol. Chem.*, 1913–14, **16**, 187) for the determination of amino acid nitrogen in animal tissues are long and tedious, call for large tissue samples, and involve the use of alcohol; also there are grounds for believing that some of the amino acids are lost in the treatment with alcohol. A method is now described which is free from these disadvantages. It is a modification of the technique of Greenwald (*J. Biol. Chem.*, 1915, **21**, 61), Bock (*J. Biol. Chem.*, 1916–17, **28**, 357) and Blau (*J. Biol. Chem.*, 1923, **56**, 861) for the determination of the amino acid content of blood, and has been used primarily for the analysis of the liver and muscle of rabbits and rats. The procedure is as follows:— Approximately 4 to 5 grms. of tissue are excised and dropped into a mortar which contains liquid air. The sample is thus kept frozen, while being finely powdered, and at a temperature at which *post-mortem* changes proceed very slowly. Three grms. of the powder are then rapidly weighed out to the nearest mgrm., and transferred quantitatively with boiling 0·01 *N* acetic acid to a tube, 8 × 1 inches, graduated to 50 c.c.; 30 to 35 c.c. of the acetic acid are used in several portions of 5 to 10 c.c. each. The tube is promptly immersed in a water-bath and left for 7 minutes after the temperature of the tissue suspension has reached the boiling point. From time to time it is shaken while boiling. The tube is removed from the bath, allowed to cool, and then 3 c.c. of 50 per cent. trichloroacetic acid are added, and the volume is accurately made up to 50 c.c. with water. The suspension is thoroughly mixed and left for 30 minutes, when 2 grms. of infusorial earth are added, and the mixture is shaken for 10 to 15 seconds and filtered. Of the filtrate (37 to 38 c.c. are quickly obtained), 35 c.c. are measured into a 100 c.c. beaker, evaporated over a free flame, or on a hot plate, to about 10 c.c., and 10 per cent. sodium hydroxide (about 10 to 20 drops) is added until the solution is alkaline to phenolphthalein. Boiling of the alkaline solution is continued for 2 minutes, and it is then acidified with excess of glacial acetic acid and concentrated carefully to about 1 c.c. The residue is washed into the Van Slyke apparatus for determination of the amino acid nitrogen. The reasons for each step of the procedure and the results of various experiments are given.

P. H. P.

The Metabolism of Amino Acids. J. M. Luck. (*J. Biol. Chem.*, 1928, **77**, 13–26.)—It has previously been shown by Seth and Luck (*Biochem. J.*, 1925, **19**, 366) that the intestinal absorption of glycine and alanine by rabbits was followed by pronounced amino-acidaemia. Other amino acids, when administered in similar amounts, provoked smaller increases in the amino nitrogen content of the blood. Glutamic acid and aspartic acid were absorbed with but a slight amino-acidaemia. A report is now given of changes in the amino acid content of blood, liver and muscle following the oral administration of amino acids. The object of the experiments was to determine the relationship, if any, which existed between the

degree of amino-acidaemia obtained and the concentration increase of the amino acids in liver and muscle. The findings proved to be of a somewhat unexpected nature. The amino nitrogen content of the blood was determined by the method of Folin (*J. Biol. Chem.*, 1922, **51**, 377), and that of the liver and muscle by the method of Luck (*J. Biol. Chem.*, 1928, **77**, 1), described in the preceding abstract. Results show that when amino acids are administered to rats, *per os*, and in equimolecular amounts, increases of varying magnitude are observed in the amino acid content of liver, but no appreciable change, except with glycine, is observed in the amino acid content of muscle. With glycine the amino nitrogen content of muscle increases slowly and uniformly, and the accumulation proceeds much more slowly than it does in the liver. Although glycine and alanine increased in the same measure the amino acid content of the systemic blood, the former provoked a great increase in the amino nitrogen content of liver, whilst the latter caused no significant change. In most cases no appreciable changes were observed in the ammonia content of liver and muscle. These results are discussed, together with the closely related work of others. P. H. P.

Occurrence of Labile Phosphorus in Various Kinds of Muscles. L. Irving and P. H. Wells. (*J. Biol. Chem.*, 1928, **77**, 97–113.)—The nature of the origin of labile phosphorus in muscle (*i.e.* phosphorus set free in addition to the inorganic phosphorus already present), has not yet been established, and there are only preliminary reports to indicate the nature of its precursor. It is defined as a substance which yields acid-soluble inorganic phosphorus in acid solution, and is easily demonstrated in skeletal muscle of mammals, according to the methods defined by its discoverers. It has previously been shown by other workers that the conventional acid-soluble inorganic phosphorus does not represent the amount present in living muscle, for, by comparison of the rate of colour development in standard and extract, the initial inorganic phosphorus of frog striated muscle in ice-cold trichloroacetic acid filtrate was only about 30 per cent. of the ordinary value given by acid extraction at room temperature. This minimum was increased by fatigue, so that, apparently, muscle exhaustion caused depletion of the labile phosphorus; a muscle in rigor had likewise lost its labile phosphorus; therefore, whether or not the labile phosphorus exists in the muscle before the process of extraction, it has definite physiological significance, because of its regular variation under different physiological conditions. Labile phosphorus is now shown to be distinct from the lactacidogen of Embden (*Z. physiol. Chem.*, 1921, **113**, 138), both by definition of the conditions for determination and by the facts of its appearance. Lactacidogen occurs in smooth muscles which entirely lack labile phosphorus. In acid solution the labile phosphorus is practically completely decomposed within 30 minutes, after which time the acid-soluble inorganic phosphorus content of the extract remains constant for about a day before it shows further increase. Labile phosphorus could not be demonstrated in fish striated muscle, or in grasshopper striated muscle, or the smooth muscle generally of vertebrates and invertebrates, and heart muscle. If possibly present in any of

these muscles, its amount is of quite a different order from that in mammalian skeletal muscle. The occurrence and lack of labile phosphorus follow, in some respects, the occurrence of creatine, a natural consequence if Fiske and Subbarow's announcement of the labile compound as a phosphocreatine is substantiated. The acid-soluble inorganic phosphorus, as conventionally determined, is evidently the sum of the amount present in natural muscle and the labile phosphorus set free in acid at room temperature. P. H. P.

Effect of Temperature on the Catalase Reaction. S. Morgulis and M. Beber. (*J. Biol. Chem.*, 1928, **77**, 115–126.)—The preliminary study on the inactivation of catalase at different temperatures described by Morgulis, Beber and Rabkin (*J. Biol. Chem.*, 1926, **68**, 535) has been extended to determine the effect of variations in hydrogen ion concentration on the rate and degree of inactivation by heat. The enzyme is very slowly inactivated at temperatures below 50° C., but inactivation becomes very rapid as the temperature is raised to 55° C. or above, especially at P_H less than 6·0. It is somewhat slower at P_H more than 7·0. At P_H 4·5 the inactivation is instantaneous at temperatures above 50° C., whilst at P_H 8·0 this does not occur until 63° C. is reached. At 65° C. the enzyme is instantly inactivated independently of the hydrogen ion concentration, *i.e.* 65° C. is its critical temperature. Under proper experimental conditions the heat inactivation of catalase is an equilibrium reaction, and the point to which inactivation proceeds is determined by the degree of temperature and by the P_H of the medium. The rate of the heat inactivation follows that of a bimolecular reaction. Sucrase and amylase are most stable in the form in which they are most active, but this is not true for catalase, for the maximum stability at P_H 6·0 is in marked contrast to its rather extensive P_H range of optimum activity. Curves show the pronounced difference between the effect of P_H on the catalase *reaction* and the effect of P_H on the heat *inactivation* of catalase. Results obtained have caused the authors to return to the older conception of the amphoteric nature of catalase. The idea that catalase is an ampholyte, with an isoelectric point somewhere between P_H 4·0 and 4·5, must be definitely discarded as erroneous, as it was derived from a limited study of the catalase *reaction* at different P_H. The study of the heat *inactivation* leads one to postulate that catalase must have its isoelectric point near P_H 6·0. It must have stronger basic than acid properties. That the anion is its most vulnerable part is corroborated by the study of its heat lability. P. H. P.

Observations upon the Enzyme Asparaginase. W. F. Geddes and A. Hunter. (*J. Biol. Chem.*, 1928, **77**, 197–229.)—Asparaginase has been studied as a preliminary to an attempt to utilise it in a quantitative determination of asparagine. Experiments show that the enzyme asparaginase may be obtained by water or glycerin extraction of thoroughly disintegrated yeast cells. It is present also in the liver of the calf. It is very labile, for it is rapidly destroyed by heat and by contact with cold alcohol or acetone. It is adsorbed by kieselguhr and by ferric hydroxide, and may be precipitated by adjusting the P_H of its solution

to approximately 4·5. It may be conveniently concentrated and partly purified by precipitation with safranine, but the product thus produced is still contaminated by protease. The active enzyme obtained by the safranine method removes the amide nitrogen of asparagine quantitatively as ammonia, but leaves the amino group intact. The action of the enzyme, so far as is known, is limited to the amides of the two amino acids, aspartic and glutamic. The course of the enzymic hydrolysis of asparagine is not described by the law applicable to a simple monomolecular reaction ; coefficients of velocity calculated by that law increase as the reaction proceeds. Nearly constant coefficients are yielded by the equations— $kt=m \log \frac{a}{a-x}+x$ (in which m is an empirical constant), and $kt=\sqrt{a}-\sqrt{a-x}$. Asparaginase exerts its maximum activity at P_H 7·9 to 8·1, and its range extends on either side of this optimum to about 5·5 and 10·3. Tables and charts show the results of the experiments. P. H. P.

Insects as Test Animals in Vitamin Research. I. Vitamin Requirements of the Flour Beetle, *Tribolium confusum* Duval. M. D. Sweetman and L. S. Palmer. (*J. Biol. Chem.*, 1928, **77**, 33–52.)—Certain results are presented from a more extended study of the nutritional requirements of the confused flour beetle, *Tribolium confusum* Duval, a common pest in such human food materials as the cereals, which seem to prove the value of a phylogenetic view-point in the science of nutrition and the usefulness of this species as an experimental animal in biological analysis. It is possible to determine the vitamin requirements of this insect by the use of purified or otherwise modified rations with essentially the procedure followed with the ordinary laboratory animals. This insect can be rapidly reared on a purified ration of protein, salts, dextrin, and a small fraction of yeast, wheat germ, and their alcoholic extracts, though the latter are not so completely supplementary as the former. The addition of a fat, with or without vitamin *A*, accelerates the growth rate. Distribution of the necessary growth-promoting substance is similar to that of vitamin *B*, as defined by mammalian growth behaviour, and is, in part, identical with the purified products of the Osborne and Wakeman (*J. Biol. Chem.*, 1919, **40**, 383), and Levene and van der Hoeven (*J. Pharmacol. and Exp. Therap.*, 1926, **29**, 227) purification processes. Some evidence that a plural substance is concerned is pointed out. *Tribolium* is sensitive qualitatively to as low as 0·5 per cent. of a source of this growth-promoting substance or substances, and makes a quantitative response to its additions over a certain range. Growth on fractions of wheat, corn, oats, barley and rice indicates no absolutely limiting factor in any fraction tried. When wheat and its fractions are added to a purified basal ration which lacks vitamin *B*, the embryo and adjacent portion of the kernel are shown to be the most abundantly supplied with this factor. A similar study with maize demonstrated the presence of the necessary vitamin in the endosperm. P. H. P.

Growth on a Synthetic Ration which contains Small Amounts of Sodium. J. L. St. John. (*J. Biol. Chem.*, 1928, **77**, 27–32.)—A study has been

made of the amount of sodium required in a synthetic ration. The diet given was modified from that of Osborne and Mendel (*J. Biol. Chem.*, 1918, **34**, 131), and contained casein 18, yeast 3, agar 2, lard 5, cod-liver oil 1, starch 67, and salt mixture 4. Sodium carbonate was eliminated from the salt mixture. Calcium, magnesium and potassium carbonates and citric acid were added in powder form. The rest of the salts and the acids were added in solution. To this basic ration sodium bicarbonate was added in varying amounts to furnish rations which contained the desired per cent. of sodium. All rations were thus constant in composition, with the exception of the quantity of sodium bicarbonate used. The rats were kept on screens without bedding. Amounts of sodium below 0·3 per cent. proved inadequate for growth. With this amount of sodium growth was improved and the animals appeared in much better condition. Additional sodium was accompanied by improved growth. The best results may, in general, be expected when the ratio of potassium to sodium is low, but the level of sodium in the diet is at least as important as this ratio. The difference in the appearance of the animals was more striking than the differences in the growth curves. Rats receiving small amounts of sodium were blind in many cases. There was no reproduction on any of the rations used, perhaps owing to lack of vitamin *E*.

P. H. P.

New Differentiation between the Antineuritic Vitamin *B* and the Purely Growth-Promoting Vitamin *B*. H. M. Evans and G. O. Burr. (*J. Biol. Chem.*, 1928, **77**, 231–240.)—A new and striking differentiation has been secured between the antineuritic vitamin *B* and the purely growth-promoting vitamin *B*. Experiments on rats have been carried out with different diets, and it has been found that the concentrate of tikitiki (a dilute alcoholic extract of white rice polishings made by the Philippine Bureau of Science for distribution to the natives of the islands) possesses the antineuritic vitamin *B*, but is almost lacking in growth-promoting vitamin *B*. Growth-promoting vitamin *B* is present both in commercial maize starch and in commercial casein. P. H. P.

Toxicological and Forensic.

Composition of the Air in Paris Streets. R. Cambier and F. Marcy. (*Comptes rend.*, 1928, **186**, 918–921.)—Determinations made during February–June, 1927, on the air of busy Paris streets show that, under normal meteorological conditions, only samples of air collected at the barriers employed to regulate the traffic and at about the level of the exhausts of motor-cars, contained 1 part of carbon monoxide per 10,000 of air. In a single case 1 part in 2000 was found, this air being toxic if breathed for several hours. With samples taken at the barriers in wide streets at a height of 1·6 metres, the carbon monoxide content never exceeded 0·4 to 0·5 part per 10,000. In a narrow and busy street, the proportion of carbon monoxide diminished rapidly to less than 1 in 100,000 when the barriers were removed and the vehicular traffic moved freely. T. H. P.

Blood Group Percentages for Arabs, Armenians and Jews. E. H. R. Altounyan. (*Brit. Med. J.*, 1928, 546.)—In the course of routine blood grouping of 1758 patients at an Aleppo hospital laboratory during the last five years certain data of general interest have been obtained. In the accompanying table the Armenians and Jews represent well-defined unmixed racial groups; under the heading of Arabs a certain number of Turks, Turkomans, and Kurds have been unavoidably included. Their number is relatively small, and the analysis of a small series of " pure " Bedouin Arabs has given practically identical figures for the distinguishing Groups II and IV. It is hoped in the course of the next few years to compile a series for the Kurds, about whom, ethnologically, little is known.

Race.	Number examined.	Group I. Per Cent.	Group II. Per Cent.	Group III. Per Cent.	Group IV. Per Cent.
Arabs ..	933	61=6	345=37	194=21	333=36
Armenians ..	653	42=6	346=53	89=14	176=27
Jews	172	14=8	58=34	34=20	66=38

Note.—It will be observed from the above figures that whereas in the case of Arabs and Jews the relative proportion of Group II and IV. is as 1 to 1, in the Armenian figures the proportion is as 2 to 1.

Agricultural.

Mechanical Analysis of Heavy Ferruginous Soils. R. C. Groves. (*J. Agric. Sci.*, 1928, **18**, 200–205.)—Difficulty has been experienced in the mechanical analysis of heavy ferruginous soils, partly on account of the difficulty in obtaining a proper dispersion of the clay, and partly owing to the ease with which the dispersed clay is re-flocculated (*cf.* ANALYST, 1926, **51**, 211). The following method was found the most satisfactory of those tested:—The earth (20 grms. ground to pass a 1 mm. sieve) is moistened with water and heated on the water-bath in a porcelain dish (at least 6 inches in diameter) with 5 drops of 50 per cent. ammonia, and 20 c.c. of 6 per cent. hydrogen peroxide. When the first frothing has subsided, the additions of ammonia and hydrogen peroxide are continued till gas is no longer evolved, the mixture evaporated to a paste, allowed to cool and rubbed, gently but thoroughly, with a rubber pestle in the presence of 3 drops of ammonia. The solution is diluted to 100 c.c., stirred, and the suspended matter carefully decanted into a 2-litre beaker. The stirring and decantation are repeated twice with 50 c.c. portions of water, and the residue again triturated with a little ammonia till no more clay is separated after gentle rubbing for 3 minutes. The contents of the beaker are neutralised, brought to an acidity of 0·2 *N* with hydrochloric acid, filtered after an hour, and washed in the usual way. Mechanical shaking does not affect the results, and may be omitted. In this case the residue is shaken by hand in a 1000 c.c. cylinder with 50 c.c. of 10 per cent. ammonia, and the fractions determined by the pipette method. The method causes the solution of a small amount of mineral matter which would ordinarily be included in the " loss by solution in hydrochloric acid." J. G.

Determination of the P_H Values of Turbid Soil and other Solutions. C. D. Gadd. (*J. Agric. Sci.*, 1928, **18**, 206–208.)—On adding ten drops of each of a suitable range of buffer solutions to 5 c.c. portions of an extract of the soil and about 0·6 c.c. of indicator solution, the P_H value is that of the buffer solution, which produces no change in colour when compared with that of a control to which 10 drops of distilled water have been added. The method overcomes the difficulties due to coloured or turbid solutions, and the colour may be viewed through one tube only. The extract is prepared from 2 parts of water and one part of soil, shaken for 10 minutes, and allowed to settle for 24 hours. Filtration may cause an error of as much as 0·5 P_H, even if the first 25 c.c. of filtrate are rejected. Brom-cresol purple has been found useless for certain soil solutions.

J. G.

Rapid Determination of the Phosphoric Ion in Soils and Fertilisers by Ceruleo-molybdimetry. G. Denigès. (*Comptes rend.*, 1928, **186**, 1052–1054.)—The molybdic reagent employed is prepared by mixing 10 per cent. ammonium molybdate solution with an equal volume of concentrated sulphuric acid, diluting the mixture fourfold with water, leaving it in contact for an hour, with occasional mixing, with 0·3 grm. of copper turnings in a flask almost filled by the liquid, and decanting off the clear reagent.

To determine the phosphoric ion in a soil, 5 grms. of the prepared sample are shaken repeatedly in a stoppered flask with 50 c.c. of water during 15 minutes and filtered. Five c.c. of the filtrate are heated to boiling point with 8 drops of the molybdic reagent, boiling being maintained for 12–15 seconds. The blue coloration thus developed is compared with those obtained similarly with a series of solutions containing from 0·002 to 0·012 grm. P_2O_5 per litre ; dilution of the soil extract, or the use of a scale corresponding with quantities of 0·0004 to 0·002 grm. P_2O_5 per litre, may be necessary in some cases. If the soil extract is coloured, 10 c.c. of it are acidified with one drop of sulphuric acid, heated just to boiling, and placed in front of the standard tube.

To determine the phosphoric ion soluble in dilute mineral or organic acids, more dilute solutions must first be tried. If 2 per cent. nitric acid solution is employed, 5 grms. of the soil are treated with 50 c.c. of the acid (or more with a highly chalky soil) and the liquid filtered. The filtrate is diluted twenty-fold and treated as above, but with 10 drops of the reagent. If either nitric acid of greater concentration than 2 per cent. or *aqua regia* is used to extract the soil, 1 c.c. of the filtrate is evaporated to dryness and the residue calcined and dissolved in 10 c.c. of boiling water containing 1 drop of sulphuric acid. The cold liquid is made up to 20 c.c., and the determination carried out on 5 c.c. This procedure is followed also when citric acid solution is used for extracting the soil, the calcination being preceded by addition of a few drops of nitric acid.

With a ferruginous soil which does not give up more than 1 or 2 per cent. of its weight of iron to the solvent, the operations are carried out similarly, except that 12 drops of the molybdic reagent are used. If the iron is more abundant, the colorimetric test must be made by adding 10 drops of a solution containing

2·5 grms. of ammonium molybdate and 25 c.c. of concentrated sulphuric acid per 200 c.c., and boiling the liquid for 30 seconds with 10 to 13 grms. of copper turnings. By this means the molybdic reagent reduces the iron to the ferrous state, and is converted to its original condition by the excess of copper present. The standard colorations must be prepared similarly. Good results are then obtained in presence of even 50 per cent. of iron.

With fertilisers the determinations are made in the same way, but higher dilutions are necessary owing to the higher proportions of phosphate present.

T. H. P.

Organic Analysis.

Mixed Fatty Acids in Head and Blubber Oils of the Sperm Whale. T. P. Hilditch and J. A. Lovern. (*J. Soc. Chem. Ind.*, 1928, **47**, 105–111T.)—An examination of the head and blubber oils of the Antarctic sperm whale showed in 100 grms. of oil :—Alcohol content : sperm head oil, 39·3 ; sperm blubber oil, 33·6 ; fatty acids equivalent to alcohols, 36·9 and 34·2 ; combined as wax esters, 73·4 and 65·7 ; balance of fatty acids isolated, 25·1 and 31·8 ; as triglyceride, 26·5 and 33·3 ; approximate composition : wax esters, 73·5 and 66·0 ; glycerides, 26·5 and 34·0 per cent. The head oil is less unsaturated than the blubber oil, but neither contains much fatty acid which is less saturated than monoethylenic. The fatty acids from the blubber contain unusually much palmitoleic acid, and a considerable amount of unsaturated acids of the C_{20} series, the highly unsaturated derivatives of this series, characteristic of ordinary whale oil, being absent. The head oil fatty acids consist of over 50 per cent. with lower molecular weight than palmitic acid ; 3–4 of capric ; 16 of lauric ; and 14 per cent. of myristic acid, and the corresponding monoethylenic lauroleic (4 per cent.) and myristoleic acids, 14 per cent. The monoethylenic acids do not appear to be identical with the most commonly occurring forms in animal and vegetable fats. D. G. H.

Constituents of the Unsaturated Fatty Acids of Chrysalis Oil. W. Kimura. (*J. Soc. Chem. Ind., Japan*, 1927, **30**, 223B.)—The sample of silk-worm chrysalis oil examined had the following characteristics :—Sp. gr. at 20°/4° C., 0·9259, n_D^{20}, 1·4707 ; iodine value, 132·4 ; acid value, 8·54 ; saponification value, 192·2 ; insol. fatty acids, 96·05 per cent. ; and unsaponifiable matter, 2·08 per cent. The lead salt and alcohol process was used to separate the unsaturated acids, which were then brominated, and the ether-insoluble hexabromide separated. The residual oily bromides were boiled with petroleum spirit, washed with the same solvent and weighed. The following hydroxy acids were prepared :—Dihydroxystearic acid (m.p. 132° C.), α-sativic acid (m.p. 156° C.), β-sativic acid (m.p. 173° C.), and linusic acid (m.p. 203° C.). From the results obtained the liquid fatty acids were calculated to consist of 21·3 per cent. of linolenic, 48·9 per cent. of linolic, and 29·8 per cent. of oleic acid. R. F. I.

Reaction of Caryophyllene. D. T. Gibson. (*J. Chem. Soc.*, 1928, i, 750–751.)—When a solution of diazo-acetic ester in caryophyllene (b.pt. 124° C. at 12 mm., n_D^{14}, 1·5012) is added gradually to an excess of caryophyllene at 180 to

200° C. in the presence of finely divided copper, a *cyclo* propane ester (b.pt. 130 to 160° C. at 2 mm.) may be separated (*cf.* Deussen, *J. prakt. Chem.*, 1927, **117**, 282). This ester may be hydrolysed by a 10 per cent. alcoholic solution of potassium hydroxide, and the potassium salt decomposed with acid after removal of the alcohol and uncombined oil by steam distillation. The *cyclo* propane acid, $C_{16}H_{25}.COOH$ (m.pt., 165° C.; $[\alpha]_{5461} -40°$ in alcohol), may be crystallised from petroleum spirit, benzene or acetic acid, and is stable to bromine in chloroform, and only slowly attacked by a boiling acid solution of potassium permanganate. The mother liquors contain a resinous acid which is the sole product of hydrolysis by more concentrated alkali. The test may be confirmed by the preparation of Wallach's caryophyllene alcohol, m.pt. 94° C., and has been applied to a fraction of supa oil. J. G.

Inorganic Analysis.

Adipic Acid as an Original Standard in Alkalimetry. F. T. Van Voorst. (*Chem. Weekblad*, 1928, **25**, 22–23.)—Commercial adipic acid, recrystallised from five times its weight of distilled water and dried at 130° C. has m.pt. 152·0±0·1° C., density 1·366±0·003 (at 12·5° C.), and an equivalent weight of 72·99 (corrected for the buoyancy of the air). Since it is not hygroscopic and its purity is easily controlled from its m.pt., it is superior to many other acids or acid salts for the standardisation of sodium hydroxide solutions. Comparative titrations with a number of such substances confirmed this, and demonstrated the unreliability of oxalic acid either as $C_2H_2O_4,2H_2O$ or in the anhydrous state. The acid is dissolved in hot water, and used with phenolphthalein as indicator. J. G.

Detection and Determination of Barium, Calcium and Strontium. O. Macchia. (*Chem. Zeit.*, 1928, **52**, 281–282.)—Barium, calcium, and strontium may be detected in the mixed carbonates by dissolving them in dilute hydrochloric acid, concentrating to 8–10 c.c. if necessary, and dividing the liquid into two portions, which are treated as follows: (1) This portion is shaken with 0·5 grm. of malonic acid until solution is complete, slight excess of ammonia solution being added, and the liquid again shaken vigorously. The presence of barium is indicated by the formation of a white precipitate of barium malonate, which is filtered off. The filtrate is warmed with 4 to 5 times its volume of methyl alcohol (not necessarily very pure) and left for 15 to 20 minutes, strontium malonate being almost quantitatively, and calcium malonate partially, precipitated. The precipitate is filtered off through a pleated filter and washed with aqueous methyl alcohol. The filtrate is very carefully heated with 20 per cent. potassium cyanate solution, and is closely observed to note the formation of white flocks of calcium cyanate, which gradually disappear. If strontium, but not calcium, is present, the solution becomes somewhat turbid on addition of the cyanate. (2) A more rapid procedure consists in neutralising the liquid with ammonium hydroxide and shaking it with 4 to 5 times its volume of potassium ferrocyanide solution (55 to 60 per cent. of

the hydrated salt) at 80–90° C. ; in presence of calcium a white crystalline precipitate of $CaK_2Fe(CN)_6$, $3H_2O$ is formed. The cold liquid is filtered, and the filtrate diluted, rendered alkaline with ammonia, heated to boiling, and treated with potassium chromate, yellow barium chromate being precipitated if barium is present. With the filtrate from this, sodium carbonate solution at 80–90° C. gives a white precipitate if strontium is present.

The determination is carried out as follows :—The neutral or faintly acid solution of the mixed chlorides is mixed with hot (80–90° C.) saturated potassium ferrocyanide solution, the mixture being stirred until cool. The precipitated potassium calcium ferrocyanide, which separates slowly if the calcium is in small amount, is collected on a small tared filter and washed with saturated potassium ferrocyanide solution, the filtrate and washings being mixed. The filter and precipitate are stirred with hydrochloric acid, and the liquid diluted with water until the precipitate which forms redissolves, made alkaline with ammonia, heated to 80–90° C., treated with *N* ammonium oxalate solution and, after standing, filtered. The precipitate of monohydrated calcium oxalate is thoroughly washed, dried, ignited and weighed as calcium oxide. The solution, filtered from the potassium calcium ferrocyanide, is diluted, rendered alkaline with ammonia, heated to 80–90° C., and treated gradually with 0·5 *N* potassium chromate solution, the precipitated barium chromate being filtered off and washed with the potassium chromate solution. The filter is placed in a beaker containing dilute hydrochloric acid, which is well stirred to dissolve the precipitate, and is then diluted, boiled, and treated with a few c.c. of *N* ammonium chloride solution, two or three crystals of potassium chlorate and dilute sulphuric acid. The liquid is boiled for 15–20 minutes and filtered, the barium sulphate being washed, dried and weighed as usual. The filtrate from the barium chromate is boiled and treated with *N*-sodium carbonate solution, the precipitated strontium carbonate being filtered off, washed with water, dried and ignited to give the oxide. The percentage of strontium thus found should be increased by 0·2, as a small proportion is carried down as chromate with the barium chromate. T. H. P.

Iodimetric Vanadium Determination in Steel and Ferrovanadium. K. Roesch and W. Werz. (*Z. anal. Chem.*, 1928, **73**, 352–355.)—It has been shown that iodide reduces vanadium pentoxide only to the tetroxide stage if phosphoric acid is present. This fact is utilised in the following processes. *Ferrovanadium* (1 grm.) is fused in a nickel crucible with sodium hydroxide (10 grms.) for 20 minutes, first with a small flame, then to redness. The product is leached with hot water, the liquid filtered into a graduated 500 c.c. flask, and 50 c.c. pipetted into a 300 c.c. conical flask ; 75 c.c. of phosphoric acid (1·7) are added, and, after cooling, potassium iodide. After 5 minutes the liquid is titrated with 0·05 *N* thiosulphate solution (1 c.c.=0·00255 grm. V.). Starch is added towards the end. *Steel* : 3 to 5 grms. are dissolved in 30 to 50 c.c. of hydrochloric acid with the addition of nitric acid ; the liquid is concentrated to 25 c.c. Any tungstic acid is filtered off, and the filtrate extracted with ether. The latter is freed from

traces of vanadium with a little hydrogen peroxide. The aqueous liquid is evaporated, the residue dissolved in 20 c.c. of nitric acid (1 : 1), diluted, treated with a few c.c. of 10 per cent. manganous sulphate solution, and precipitated with ammonia. The washed precipitate is ignited in an iron crucible and fused with 3 to 4 grms. of sodium hydroxide in a current of hydrogen (perforated crucible lid) : the vanadium is converted into vanadate whilst chromic oxide is not oxidised. The product is dissolved in 50 c.c. of water, the solution filtered, and the residue washed with hot water ; the filtrate is titrated as before. W. R. S.

Separation of Ceria from other Rare Earths. J. W. Neckers and H. C. Kremers. (*J. Amer. Chem. Soc.*, 1928, **50**, 955–958.)—Cerium is separable from its congeners because it is oxidisable to the quadrivalent state. Anodic oxidation accomplishes a 90 per cent. oxidation in the case of the sulphate or nitrate, but not chloride. In presence of sodium phosphate gradual addition of permanganate to a nitrate solution of the rare earths containing 5 per cent. of free acid causes quantitative precipitation of ceric phosphate, a heavy, cream-coloured precipitate insoluble in dilute acid, decomposed by sodium hydroxide ; the latter can be dissolved in nitric acid and cerous oxalate precipitated by addition of oxalic acid. The other rare-earth phosphates are soluble in the 5 per cent. acid. Thorium, if present, is also precipitated as phosphate : the rare earths from monazite may thus be freed from cerium and thorium by a single precipitation. W. R. S.

Fractional Precipitation of the Rare Earths by Electrolysis. J. W. Neckers and H. C. Kremers. (*J. Amer. Chem. Soc.*, 1928, **50**, 950–953.)—Electrolysis of neutral salt solutions of the rare earths results in precipitation of the hydroxides at the cathode. As the basicity of the rare earths decreases with increasing atomic weight, a fractionation is possible in principle. The fractional separation of lanthanum and praseodymium was investigated : an 8 per cent. solution (15 litres) of the chlorides, after 50 hours' electrolysis, during which eleven fractions were removed, gave a residual fraction containing 99 per cent. of lanthanum. When applied to a mixture of all the ceria earths containing a small amount of yttria earths, the process was efficient only in regard to concentration of the lanthanum, though the yttria earths and samaria concentrated in the first fractions. The fractionation of praseodymium and neodymium was attempted, but no appreciable separation was achieved. W. R. S.

Analysis of Samarskite. R. C. Wells. (*J. Amer. Chem. Soc.*, 1928, **50**, 1017–1022.)—Observations and suggestions are made for improved separation of the constituents of the precipitates obtained in Lawrence Smith's hydrofluoric acid process. The author determines niobium volumetrically by Metzger and Taylor's method, having now adopted a factor of " about " 0·00755 grm. Nb_2O_5 per c.c. of 0·1 *N* permanganate (*cf.* Schoeller and Deering, ANALYST, 1927, **52**, 631). Sears' method for the separation of tantalum and niobium (*ibid.*, 1926, **51**, 215) proved unreliable as a quantitative method. W. R. S.

Reviews.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. By the Editors and the following contributors: W. A. GALLUP, HANS EDWARD FIERZ-DAVID, A. W. JOYCE, and H. E. FIERZ-DAVID and V. E. YARSLEY. Pp. ix+658. London: J. & A. Churchill. 1928. Price 30s.

The new volume of *Allen's Commercial Organic Analysis*, with the exception of the first section dealing with colorimetry (18 pp.), is entirely occupied with the formation, structure and analysis of the synthetic dyes, and thus differs markedly from the most nearly corresponding volume (Vol. V) of the fourth edition, which in its 704 pages included sections on tannins, natural colouring matters and inks. In view of the fact that much of the material concerning dyestuffs was contributed by the present writer to the fourth edition, reviewing this work has proved of more than usual interest.

The first section of 18 pages, contributed by Dr. W. S. Gallup, is devoted to colorimetry, and after an explanation of the practical application of Beer's Law of Absorption, various forms of colorimeter are described. Regarding the bibliography on p. 18, the reviewer thinks that dates of references should always be given.

The next section, Dyes and Colouring Matters, which is by Professor Fierz-David of Zürich, occupies 394 pages, or more than half the book. Division of dyes according to their affinity to fibres has been completely abandoned, and classification is on purely chemical lines. As a chemist, the reviewer is in favour of this alteration, though it must be admitted that, from the standpoint of the dyer, much may be said for classification of dyestuffs as substantive, adjective,etc.

The author divides the dyes into the following classes:—(1) Nitroso and Nitro; (2) Azo; (3) Stilbene; (4) Pyrazolone; (5) Carbonium; (7) Acridine; (8) Quinoline; (9) Thiazole; (10) Indamine, Indophenol and Indoaniline; (11) Azine; (12) Oxazine; (13) Thiazine; (14) Sulphur; (15) Hydroxy-ketone; (16) Anthraquinone; (17) Indigo(id). The missing sixth class is evidently that of the xanthenes, as is seen on reference to p. 255. In dealing successively with the classes enumerated above, a short account is given of the general characteristics and structure, followed by the analytical characteristics of individual members of each class. Considerable alteration will be observed in these tables; in the fourth edition the practice was to give in columns the name of the dye, its structural formula, remarks as to method of formation, character of the dyestuff, *i.e.* its appearance as a solid and in solution, the reaction of the aqueous solution with sodium hydroxide and hydrochloric acid, the colour of the solution in concentrated sulphuric acid and change on dilution and, lastly, other characteristics. In the tables of the present edition, the first column gives the commercial name or names of the dyestuff, followed by the chemical name and figures giving the numbers in Schultz's Farbstoff-Tabellen and the Colour Index. The formula is omitted.

The second column gives analytical characteristics, whilst a third column is used occasionally for further remarks. The data given in the second column are generally much fuller than those in the previous edition, where they were frequently too scanty owing to the general arrangement and lack of space; the reviewer recognised this when writing portions of the fourth edition. The lack of constitutional formulæ for the various dyes will probably be a source of difficulty to some users of the tables, especially those who are not constantly working with synthetic dyestuffs.

The third section of the work, The Synthetic Dyestuffs, by Dr. A. W. Joyce, deals largely with the constitution of the different classes of dyestuffs and the methods used in their preparation. To a certain extent overlapping of the second and third sections has been unavoidable, and, whilst both authors nominally use the same clasification, it may be noted that Dr. Joyce, while classifying the triphenylmethane dyes under the head of carbonium colouring matters, actually writes their structures as quinonoid ammonium salts (*e.g. Victoria Blue B*, p. 446).

The identification of azo-dyes is also included in this section, and the methods used for identifying the fission-products of reduction are explained. In dealing with the properties of these products, the author remarks (p. 547), that in many cases data could not be found in the literature.

In the short fourth section (pp. 613–631), Professor Fierz-David and Dr. V. E. Yarsley deal with the Analysis of Colouring Matters, and an extensive bibliography of the subject is given. They state that their contribution must be considered as an epitome of the methods available for the analytical investigation of colouring matters. As the authors remark, "the standard work on this subject, to which reference is continually made, is *The Analysis of Dyestuffs* by Arthur G. Green (Griffin, London, 1920). Most of the other books dealing with the analysis of dyestuffs, both from the English and foreign press, are merely reproductions of this work, either with or without the consent of the author."

The task the authors have undertaken is no easy one and has been carried out well. Printing and paper are excellent and misprints comparatively few, though some of the structural formulæ in the third section need attention (*e.g.* pp. 446, 465).

J. T. HEWITT.

BIOCHEMICAL LABORATORY METHODS FOR STUDENTS OF THE BIOLOGICAL SCIENCES. By C. A. MORROW, Ph.D. Pp. 350+xvii. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 18s. 6d. net.

Although numerous books on biochemical laboratory methods for medical students appear at frequent intervals, books for chemical work adjusted to the requirements of students in the faculty of science are rare. Professor Morrow's book is, therefore, a welcome addition to plant biochemistry, especially as it is based upon a practical laboratory course given by the author for a number of years in the Division of Agricultural Biochemistry at the University of Minnesota.

The 233 experiments chosen by Dr. Morrow provide the student of the biological sciences with an excellent training in plant chemistry, as well as an introduction to biochemical research, as each separate experiment is provided with a good and extensive bibliography. Both analytical and synthetical methods are well selected. The character of the book is best illustrated by Experiment 106, which gives the synthesis of amino acids. Glycine has been chosen as the illustration. A detailed description of the preparation of glycine, covering a page, is given, and this is followed by a bibliography of seven papers; of these, one is of historical interest, three relate to amino acids in general, and the remaining three are devoted to the chemistry of glycine in particular. The details as to the preparation of glycine are good, and the writer of the review has had the experiment repeated, with excellent results.

The general chapters are also well written, especially those on colloidal chemistry, the carbohydrates and the enzymes, and there is no doubt that Professor Morrow's book will be found useful in any library on plant chemistry.

M. NIERENSTEIN.

A TEXTBOOK OF BIOCHEMISTRY FOR STUDENTS OF MEDICINE AND SCIENCE. By A. T. CAMERON, M.A., D.Sc., F.I.C. Pp. x+462, with 12 figures. London: J. & A. Churchill. 1928. Price 15s.

The author has arranged his book in various parts, starting with an introduction, catalysis and hydrogen-ion concentration, and continuing with the foodstuffs, digestion, intermediate metabolism, reproduction and quantitative metabolism. There are also addenda devoting a few pages each to the chemistry of immunology, and biochemistry in industry and pharmacology.

In his preface the author states that the incompleteness of our present knowledge has led him to choose this order of arrangement, which is not completely logical, but which is most suitable for teaching. As the book is intended mainly for medical students, the method which has been selected is probably the best, but for the chemist it is rather disconcerting, since discussions on subjects such as carbohydrates, proteins and enzymes appear in each portion of the book. The difficulty of co-ordinating chemical information in this way has led the author into one or two errors; thus, on page 80, he does not even mention ergosterol among the sterols, and suggests that vitamin *D* is related to cholesterol, whereas on p. 362 he states definitely that the vitamin can be obtained by the irradiation of ergosterol. At times he is apt to cling to old theories ; he gives the various stages for the degradation of starch through erythrodextrin and achroodextrin, and believes that diastase, which is responsible for the hydrolysis of starch to maltose, is only one enzyme. On another page he gives the enzymic cycle (maltose maltase glucose maltase isomaltose emulsin glucose emulsin maltose) as correct, and later assumes that Abel's work on crystalline insulin is definite.

Prof. Cameron is not without a sense of humour, and shows, by the stand which he makes for alcohol, that he is not a prohibitionist. Therefore, when he claims that Biochemistry is the offspring of Physiology, he might, considering

the work of Pasteur, Lindner, the Browns and others, with truth have said that it drew its first sustenance from beer.

The book serves as a very good introduction to the study of biochemistry, as a whole, but is not intended to replace works such as the series of monographs edited by Sir F. G. Hopkins and Prof. Plimmer.

Messrs. Churchill are to be congratulated on presenting an attractive and well-printed book at a moderate price.

T. McLachlan.

The Microscopy of Drinking Water. By Prof. G. C. Whipple. 4th Edition, re-written and enlarged. Pp. xiv+586, 19 plates. London: Chapman & Hall, Ltd.; New York: John Wiley & Sons, Inc. 1927. Price 35s. net.

This book has already passed through three editions, a fact which definitely attests to its usefulness in dealing with the many problems which microscopic life presents to the sanitary chemist and engineer. This study—Micrology—is playing an increasingly important part in the whole science of sanitation, whether it be the disposal of sewage or the protection of water supplies. Popular standards of purity are rising, and to-day a water must not only be "safe," but also pleasant to drink; to this desirable end "micrology" is a fundamental necessity.

The present revision has been ably performed by two co-workers of the late Prof. G. C. Whipple, of Harvard University, thus securing a continuity of the author's ideas.

The work, as in previous editions, is divided into two parts. Part I, which deals with Applied Microscopy, contains 15 chapters, and occupies some 440 pages. The scope of this portion may be realised from the following abbreviated summary of its contents:

Chaps. 1–3. Micro-organisms in drinking and polluted water. Colour, turbidity, odours and tastes; Chemical analyses, reliability and errors; Odours and tastes due to organisms and chlorination by-products.

Chaps. 4–6. Collection and examination of samples. Surface and deep water bottle sampling. Plankton nets and filters. Sampling apparatus. Examination of samples, filtration, concentration, and enumeration. Quantitative units, errors. Use of microscope, camera lucida, &c. Records of examination, tabular, graphic and photographic; Central tendency and variation; Frequency and fluctuation.

Chaps. 7–10 deal with limnology or "ponded" waters, as distinct from rheology or "flowing" waters; herein are discussed the various physical, chemical, and biological factors, such as heat, wind, and light, and their effects on these waters. Vital processes and dissolved gases, photosynthesis, Plankton, its requirements and chemical composition. Dissolved oxygen and free carbon dioxide; diurnal and seasonal changes. Bicarbonates, alkalinity, nitrates, silica, and chlorides. Organic carbon and nitrogen. Plankton-, soluble-, amino-, non-amino- nitrogen. Diatoms, temperature, light. Other organisms. Seasonal variation, horizontal and vertical distribution of micro-organisms.

Chap. 10 deals with reservoir construction and water storage effects.

Chaps. 11–15 are devoted to rheology or "flowing" waters; the various physical, chemical and biological factors and their effects are discussed as under limnology. Self-purification of streams. Parameters of self-purification; Gases, oxygen, carbon-dioxide. Organic nitrogen, Oxygen demand, Bacteria, Plankton, Bottom organisms. Control of algae and water weeds. Algicides, copper sulphate, chlorine and lime. Purification of waters containing algae, covered and open filters. The concluding chapter is devoted to mico-organisms in water conduits.

The scope and thoroughness of the work have been greatly increased, but, by the efficient use of charts and tables, this has been done without unduly increasing the size of the volume. The various descriptions are facilitated by numerous detailed illustrations in the text and the frequent application of mathematical formulae, together with recent literature references, produce a well-finished and satisfactory result. It is, indeed, an excellent and thoroughly modern exposition of the problem, and should be in the possession of all interested in water supplies and river pollution problems.

Part 2. "Determinative Microscopy" is divided into 17 short chapters, which occupy 110 pages, devoted to classification, nomenclature and ecology. After the first two chapters, which afford a general review of classification and algae, each succeeding chapter is appropriated to one of the following subjects or groups: Cyanophyceae, Chlorophyceae, Xanthophyceae, Diatomaceae, Rhodophyceae, Fungi, Schizomycetes, Phycomycetes, Protozoa, Rotifera, Crustacea, Bryozoa, Porifera, Miscellaneous organisms. The final chapter deals with the ecological classification of micro-organisms, and contains a list of some thousand organisms so classified. A glossary of scientific terms, indexes and 19 coloured plates complete the volume.

The many difficulties inseparable from nomenclature classification and synonymy have not been entirely surmounted; thus on page 544 the whole of the Pinnularia group has already appeared under Navicula, and similar confusion has occurred in other groups, which need some little correction.

The nineteen coloured plates which conclude the volume have appeared in previous editions. They are of variable excellence, and, in the event of a future edition, it might be desirable to separate the various groups more completely. Plate IV, Figures 1, 3, 4, and Plate XI, Figure 3, are unsatisfactory. The general absence of specific titles disarms criticism, but Plate VII, Figures 9 and 10, are scarcely satisfactory; the former is not characteristic, and the latter belongs to another genus. It might be advisable to restrict future illustrations to those species given in the ecological list.

Considering the small space allotted to this section, a remarkably clear and concise account of the whole subject has been given. The numerous dichotomous keys should assist determination, and the last chapter should do much to stimulate similar efforts in this country. It should be realised that the above criticisms

on the specific details of the work will naturally appeal less forcibly to American workers than to us.

Typographical errors are infrequent; "planktic" is usual in American works, for "planktonic," but it is unfortunate that by a very similar contraction "parthogenetic" occurs twice in the glossary, although correctly spelt in the text.

Analysts will note that the dissolved oxygen table on page 193 differs from the well-known data of Roscoe and Lunt and also from a later table by Dr. Fox. The values given, however, agree closely with the mean values of these data.

J. W. HAIGH JOHNSON.

TECHNICAL METHODS OF ORE ANALYSIS. By ALBERT H. LOW, Sc.D. Tenth edition. Pp. 348. Chapman & Hall, Ltd. Price 17s. 6d. net.

The tenth edition of Low's Technical Methods is found, upon comparison with the original work, first published in 1905, to contain new matter, as well as a revised and extended treatment of the older contents.

New chapters on fluorine, molybdenum, the testing of oil shales, together with an inclusion of methods applied to the analysis of alloy steels and bearing metals, short notes upon miscellaneous analysis, methods of the Committee of the American Chemical Society on Coal, are some of the features which mark an extension of boundaries.

Low's work projects personality. However much methods may be "standardised," there is room for originality; and whilst fundamentals may vary but slightly, variants of working methods stamp the man. On reading the book, one is again acutely conscious of the fact that Analytical Chemistry is, or ought to be, the work of a craftsman.

For the advanced student there is, in this treatise, a wealth of minute detail attached to each operation and which cannot fail to inspire confidence and foster a desire to try methods previously unknown to him.

To the tyro, abstraction of the methods given, and a self-imposed sifting of the various principles to be applied, might well supplement a modern training along the lines of earlier chemists whose school demanded trial and rejection or adoption.

The more experienced chemist will find much material for consideration, and, in many instances, surely garner direct additions to his working outfit, and, whilst all collections of working methods tend to be provocative, it is this latter process which makes for progression.

The book deals with many of the metals and non-metallic elements, and there are also chapters on testing crude petroleum, boiler waters and electrolysis, in addition to those previously mentioned.

The book can be recommended with confidence.

GEO. R. THOMPSON.

GENERAL MICROBOLOGY. By WARD GILTNER. Pp. xvi+471. London: J. and A. Churchill. 1928. Price 15s. net.

The author has selected the title "Microbology" as indicating more correctly a discourse upon microbes in general (microbe-ology) than the more usual title Microbiology. The book is primarily intended as an elementary text-book for second and third-year students, and the author's aim has been to give some account of all kinds of microbes, from filter-passers to protozoa, from all points of view—general, agricultural, industrial, and medicinal—rather than to give a detailed account of any particular branch of this science. No detailed description of laboratory technique is, therefore, given, the reader being referred for such information to any of the standard books in common use.

The book is divided into three parts as follows:—Division I, Morphology and Culture; Division II, Physiology; and Division III, Applied Bacteriology. The last occupies the main portion of the book.

Division I includes classification; occurrence; size; variations of form; reproduction; spore formation; structure; and life cycles. A good diagrammatic illustration of the relative magnitudes of bacteria, filter-passers, colloidal particles, and molecules of starch and chloroform is given, and a good general account of bacteriophage.

Division II includes an account of the functions of the cell; metabolism; microbial food; products of metabolism; physical, chemical and biological influences on microbial life.

Division III deals with microbes in the air; microbes in water; sewage disposal; soil microbes; dairy bacteriology; manufactured milk products; the alcoholic fermentation industry; other fermentation industries; infection (in general terms); [from this point onwards the subject-matter becomes more advanced, hitherto it has been elementary] immunity and susceptibility; bacterial infections of man and animals (6 chapters); diseases of man and animals caused by protozoa; and, lastly, microbial diseases of plants.

Generally speaking, these chapters are very well written; Professor Giltner possesses a fluent pen and intimate knowledge of his subject, and his descriptions are very clear and easy to follow. His chapter on immunity and susceptibility is particularly good. His book is well up to date; the Dick's streptococcus of scarlet fever and the Dick reaction are briefly, but well, described. The various pathogenic micro-organisms receive in turn a brief but good description, including morphology, cultural characteristics, biochemical reaction, and the nature of the diseases which they cause.

The section on Food Poisoning is disappointing; the Salmonella group of bacteria are not mentioned as causative agents under this heading. In dealing with the Salmonella group, however, the author quite rightly states that severe and even fatal food poisoning is caused by *S. enteritidis*, and that food poisoning due to *S. suipestifer* has been reported, but he says nothing about its being caused by

B. aertrycke, nor about the heat-stable toxin produced in food by this organism, so that, even after cooking, the poison is still potent, though the bacilli are killed. Moreover, he groups together *S. Schottmülleri* (*B. paratyphosus B.*), *S. paratyphosus* (presumably *B. paratyphosus A*) and *S. aertrycke* as causative agents of paratyphoid fever, whereas only the two former are the true causative agents, and the last gives rise to the entirely different systemic condition recognised as bacterial food poisoning.

Only three of the five serological types of *B. dysenteriae Flexner* are given.

Professor Giltner is to be congratulated upon the production of an excellent book which should prove not only very useful as an introduction to the science of general "microbology," but also of considerable interest to senior students and other readers. The book is well printed, free from printers' errors (there is a slight error on page 304, line 29, probably overlooked in proof correction), and has a good index.

D. R. Wood.

Oils, Fats and Fatty Foods. By E. R. Bolton, F.I.C. Pp. xiv+416, with 12 plates and 34 illustrations. London: J. and A. Churchill. 1928. Price 30s.

The first edition of this book, by Bolton and Revis, was reviewed in The Analyst (1913, **38**, 50). The new edition, for which Mr. Bolton is solely responsible, has not only been increased in size (by 45 larger pages), but, as the change in its title suggests, has also had its scope extended. The author has been well advised to make this change, since, apart from the question of euphony, it is not an easy matter to restrict a work of this kind within the limits covered by the term "fatty foods." At the same time, the general features of the original work have been retained.

After a general introduction dealing with the objects of the analysis of oils and fats and their products, and with the necessity for using standardised apparatus and reagents, a chapter is given to the preliminary examination of a material, including sampling, extraction of fat, determination of moisture, and detection and determination of metallic and other impurities.

The next chapter, which occupies 53 pages, gives an excellent descriptive outline of general analytical methods, which is particularly useful because it shows the author's mode of working. The methods, which are well chosen, include the determination of the usual constants and of individual constituents of fats. In this connection a slight slip may be noted on p. 64, where the method of determining stearic acid is attributed solely to Hehner, although it was the joint work of Hehner and Mitchell, as is stated on p. 137.

The following chapter, on the interpretation of analytical results, is one of the most valuable in the book. It is one thing to get accurate figures; it is quite another to know what they indicate, and here the author's wide experience in the analysis of commercial samples of oils and fats enables him to give sound reasons for the conclusions to be drawn from the data.

In Chapter V there is a description of manufacturing processes, which, without going into too much detail, gives sufficient information to enable the effects of variations in the methods of production on the composition of an oil to be followed.

In the next chapter, on butter and margarine, the author deals lucidly with a difficult problem to which he has devoted special attention, and for the solution of which he has devised new methods of analysis. Chapter VII, which deals with animal fats and marine animal oils, is not so full as other parts of the book; full justice to the fish oils can hardly be done in the three pages given to the subject.

The systematic classification in Chapter VIII gives a useful summary of the usual limits for constants and of typical values of the individual vegetable oils and fats. The botanical method of classification adopted has a logical basis, but, compared with the ordinary conventional classification, it has the disadvantage of bringing certain oils and fats into unusual juxtaposition. The plates of Miss Jesson's drawings of the various oil-bearing seeds, which formed a notable feature of the first edition, have again been admirably reproduced, and they have been supplemented by a number of excellent drawings made by Miss D. G. Hewer.

As was to be expected, the chapter on hydrogenated oils contains much original work by the author and his collaborators, and brings the subject thoroughly up to date. Chapter XI deals with cocoa, chocolate and milk chocolate; Chapter XII with feeding stuffs; and Chapter XIII with milk, giving tests and other information useful to margarine manufacturers.

Finally, the book concludes with a well-written, critical chapter on the nutritive value of edible oils and fats, including their digestibility and physiological significance, and fat-soluble and other vitamins, with methods for their determination. As this chapter, which is practically a little monograph in itself, has been written by Professor Drummond, it is hardly necessary to say that the chemist who has to examine oils and fats for accessory food factors will find here, in compact form, the authoritative information he requires.

From the foregoing outline of its contents it will be gathered that this work is essentially practical in character. The value of a book of this kind is of a different order from that of the general text-books on oils and fats, which have, perforce, to give outlines of methods of analysis which may or may not ultimately prove to be of value, and must necessarily include much that the author has been unable to test personally, whereas a book concerned with a more limited area of a vast field can afford more space for the personal touches which are looked for by other workers in the same branch of the subject.

The book under review fully answers to these requirements of a specialised work, and should, therefore, appeal to all concerned with the production or examination of edible oils and fats.

It remains to be added that the indexing and proof-reading have been efficiently done, and that the printing leaves nothing to be desired.

EDITOR.