THE ANALYST

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

An Ordinary Meeting was held on Wednesday, March 1, 1922, at the Chemical Society's Rooms, Burlington House. The President, Mr. P. A. Ellis Richards, was in the chair.

Certificates were read for the first time in favour of:—Messrs. William John Agnew, B.A. (R.U.I.); Reginald Ernest Essery, B.Sc. (Bristol), A.I.C.; Arthur Thomas Etheridge, B.Sc. (Lond.), M.B.E., F.I.C.; George Girvan Herbert, A.I.C.; and George Lewis Hutchison, B.Sc. (Lond.), F.I.C.

Certificates were read for the second time in favour of:—As an Honorary Member: Sir R. Robertson, K.B.E., F.R.S. As Ordinary Members: Messrs. Reginald Thomas Colgate, D.Sc. (Lond.), F.I.C.; Frederick Norman Appleyard, A.I.C.; Harold James Foster; Hammersley David George Holt, B.A. (Cantab.); Shozaemon Keimatsu; and James Miller, F.I.C.

The following were elected Members of the Society:—Messrs. John Leonard Lizius, B.Sc., A.I.C.; Harry Malkin Mason, M.Sc. (Sheff.), F.I.C.; Thomas McLachlan, A.I.C.; Charles March Caines, F.I.C.; and Girija Nath Mukerjee, B.Sc. (Cal.).

The following papers were read:—"The Theobromine Content of Cacao-Beans and Cocoa," by Raymond V. Wadsworth; "The Determination of Aldehydes and Ketones by means of Hydroxylamine," by Alex. H. Bennett and F. K. Donovan; "The Value of Fish Scales as a Means of Identification of the Fish used in Manufactured Products," by R. E. Essery, B.Sc., A.I.C.; "The Examination of B. P. Ointments," by Norman Evers, B.Sc., F.I.C., and G. D. Elsdon, B.Sc., F.I.C.

The Estimation of Aldehydes and Ketones by Means of Hydroxylamine.

By ALEX. H. BENNETT and F. K. DONOVAN.

(Read at the Meeting, March 1, 1922.)

THE following experiments were undertaken with the object of ascertaining whether the method described by one of us (ANALYST, 1909, **34**, 14) for the estimation of citral in lemon oil could be applied to other commonly occurring aldehydes and ketones. The process is fully described in the paper just cited, but an extended experience of its working has shown the necessity for certain precautions which may here be briefly indicated.

Commercial hydroxylamine hydrochloride frequently contains impurities which render the end point of the titration (with phenolphthalein) obscure and uncertain. To render it satisfactory for this purpose it has generally been found necessary to recrystallise it from water. Recrystallisation from hot alcohol, which is much less wasteful, does not effect a satisfactory purification.

In neutralising to phenolphthalein the sodium hydroxide should be added cautiously, any great local excess being avoided, and it is especially necessary that the liquid should not be violently agitated or allowed to stand for any length of time in presence of even a slight excess of alkali, as, in this case, a loss of hydroxylamine readily occurs (more marked in the blank experiment than in the presence of, for instance, lemon oil).

In the estimation of citral, benzaldehyde, citronellal, etc., the reaction mixture is boiled gently for half an hour under a reflux condenser. We use a round-bottomed flask of about 200 c.c. capacity, connected by a ground joint with a 25 cm. Liebig condenser fitted throughout with a Young's "rod and disc" in the manner described by Schidrowitz and Kaye (ANALYST, 1905, **30**, 190). In this way all risk of loss is avoided.

In the case of formaldehyde and acetone the reaction is carried out by leaving the mixture for two hours in stoppered bottles at the temperature of the air, and good results can also be obtained for lemon oil in this way by using double the usual amount of alcohol in order to keep the oil in solution. The results in general are within 0·1 per cent. of those found after boiling the mixture.

We have made some tests with brom-phenol blue as an indicator, but, in our opinion, the end point with methyl orange is decidedly sharper. It is, however, quite possible that some workers may find the colour change of brom-phenol blue more easy to follow. As already described, the methyl orange must be used in very dilute solution, and the tests made by spotting on a plate.

FORMALDEHYDE.—The substance used was the commercial "40 per cent." formalin solution, and estimations were made by titration with iodine, by oxidation with hydrogen peroxide and titration of the acid formed, and by the hydroxylamine process. The first two methods need no description. For the hydroxylamine

process 10 grms. of formalin were diluted to 1 litre with water, and varying quantities, from 20 to 50 c.c., were added from a burette to a mixture of 20 c.c. of 0·5 N hydroxylamine hydrochloride and 16 c.c. of 0·5 N potassium hydroxide (alcoholic solutions) contained in a stoppered bottle. After about two hours 400 c.c. of water were added, and the titration (with phenolphthalein and methyl orange as indicators) carried out in the usual manner.

The results obtained (expressed as percentage of formaldehyde in the original formalin solution) were as follows:—*By means of hydroxylamine*: 36·14, 36·14, 36·48, 36·14, 36·94; *By oxidation with hydrogen peroxide*: 36·83, 36·92.

The results with iodine were not concordant, varying with the excess of iodine employed, and, to some extent, with the time of standing.

ACETONE.—For the estimation of acetone in aqueous solution the well known Messinger method is very accurate, but in presence of ethyl alcohol the results are greatly too high. In two experiments with a solution containing 6·831 grms. of acetone and 100 c.c. of alcohol per litre we found 113·6 and 113·9 per cent. of the acetone actually present. Rakshit (ANALYST, 1916, **41**, 245) has described a modification of the method, in which baryta or lime water is substituted for potassium hydroxide, and by this he obtained more satisfactory results, but these were still rather high, especially in the presence of a large proportion of alcohol.

Some results obtained by the hydroxylamine method are shown in the subjoined table.

The acetone, after prolonged drying over calcium chloride, was redistilled with a "pear" still head and then showed a constant boiling point of 56° C. To avoid loss by volatilisation the acetone was weighed in small glass bulbs, which were then broken under water in a litre flask. One hundred c.c. of alcohol were added, and the solution diluted to 1 litre. From 30 to 50 c.c. of this solution were allowed to stand with the usual quantities of hydroxylamine hydrochloride and potassium hydroxide in a stoppered bottle for two hours at the temperature of the room.

Solution containing 6·308 grms. of acetone and 100 c.c. alcohol per litre:—
Found: 6·241, 6·240, 6·269, and 6·283; average, 6·258 =99·21 per cent.
Solution containing ·8·517 grms. acetone and 100 c.c. alcohol:—
Found: 8·544, 8·544, 8·516, and 8·510; average, 8·528 =100·1 per cent.

BENZALDEHYDE.—The preparation of the pure aldehyde with which to control the accuracy of the method presents considerable difficulty on account of the great rapidity with which it oxidises in air. The best specimens prepared from the bisulphite compound dried over calcium chloride and distilled in a current of hydrogen (only the middle fraction of the distillate being taken) and analysed immediately, gave

Taken	Found	Per Cent.
0·431 grm.	0·430 grm.	99·77
0·809 ,,	0·806 ,,	99·65
0·587 ,,	0·585 ,,	99·72

G. A. Geiger (*J. Amer. Chem. Soc.*, 1918, **40**, 1453) describes a method for the estimation of benzaldehyde by means of the phenylhydrazine compound, and, in view of the difficulty of obtaining and manipulating the pure aldehyde, uses as a standard the bisulphite compound $C_6H_5CHO.NaHSO_3, \frac{1}{2}H_2O$, which can be obtained in the pure state by recrystallisation from 50 per cent. alcohol and drying over sulphuric acid. It contains 48·39 per cent. of benzaldehyde, which is liberated by treatment with the necessary amount of sodium hydroxide, and it keeps well.

Several lots of this compound were prepared and its composition verified by estimation of the sulphur, the amount of which corresponded closely with the formula given.

The benzaldehyde was estimated by dissolving 1 to 1·5 grms. of the compound in water, adding a slight excess of sodium hydroxide, extracting the liquid three times with ether, and, after the extracts had been united in the oximation flask, carefully distilling off the greater part of the ether, adding 20 c.c. of alcohol, and treating with hydroxylamine in the usual way. Found: 47·96, 48·23 and 48·05 per cent.; calculated, 48·39 per cent.

CINNAMIC ALDEHYDE.—The aldehyde was purified by conversion into its bisulphite compound followed by distillation under reduced pressure. The fraction employed distilled at 145° C. at 30 mm.

Immediately after distillation results of 99·4 and 99·6 per cent. were obtained, but, on keeping, some oxidation soon takes place, as in the case of benzaldehyde, and after two days (in a corked tube half full of the liquid) the results were 97·2, 97·3 and 97·0 per cent.

CAMPHOR.—With camphor no quantitative results could be obtained.

CARVONE.—The carvone principally used for the trial experiments was obtained from re-distilled caraway oil by absorption with sodium sulphite solution. The oil liberated by treatment with sodium hydroxide was extracted with ether and fractionated under reduced pressure.

The fraction used in the experiments had the following values:—Specific gravity at 15·5° C., 0·9645; optical rotation at 15·5° C., 60·30° ; refractive index ($n_D^{15·5}$), 1·5006.

The following results were obtained. In each case 20 c.c. of 0·5 N potassium hydroxide solution were employed, whilst the weight of carvone taken and the time of boiling were varied.

	Carvone Taken Grm.	Time of Boiling	Carvone Found Grm.	Per Cent.
1	1·101	20 minutes	1·091	99·10
2	1·006	30 ,,	1·005	99·90
3	0·534	30 ,,	0·562	105·30
4	1·000	10 ,,	0·934	93·40
5	1·000	10 ,,	0·911	91·10
6	0·500	12 ,,	0·502	100·50
7	0·500	10 ,,	0·499	99·80
8	0·500	2 hours	0·525	105·00
9	1·005	20 minutes	1·001	99·60
10	0·598	20 ,,	0·600	100·30
11	0·499	20 ,,	0·517	103·70

It is seen, therefore, that perfectly accurate results are obtained by boiling the carvone for not less than 20 minutes with a moderate excess of hydroxylamine solution (such that about 6 or 7 c.c. of 0·5 N sulphuric acid are required for the back titration). If, however, the excess of hydroxylamine is considerably greater than this, the results are somewhat above the truth, unless the time of boiling is greatly reduced, in which case, however, with a smaller excess the action is in-complete. (See Nos. 4 and 5.)

The analyses should therefore be carried out by adding a moderate excess of hydroxylamine and boiling the mixture for 20 to 30 minutes.

Good results are also obtained by prolonged standing (overnight) in stoppered bottles at the ordinary temperature.

Carvone Taken Grm.	Carvone Found Grm.	Per Cent.
0·500	0·499	99·80
1·000	0·998	99·80

The same quantity of hydroxylamine was used in both experiments, so that in this case the varying excess has no effect on the result.

A mixture of carvone and limonene containing 48·42 per cent. of the former was analysed.

Taken 1 grm. of mixture boiled 10 minutes.	Found 48·0 per cent.
,, ,, ,, ,, left 20 hours.	,, 48·0 ,,
,, 1·992 ,, ,, ,, ,, ,,	,, 48·38 ,,

The carvone was isolated from a further quantity of caraway oil in the form of its compound with hydrogen sulphide, and the crystals obtained were dissolved in chloroform and reprecipitated by the addition of ether. As thus obtained, the melting point was 223 to 224° C.

This compound was dissolved in alcohol and treated directly with hydroxyl-amine and potassium hydroxide in the usual way, the mixture being boiled for 30 minutes. The titrations were perfectly sharp, and the following results were obtained:

Compound Taken Grm.	Carvone Found Grm.	Per Cent.
0·500	0·446	89·2
1·000	0·892	89·2
1·150	1·027	89·3
1·200	1·065	88·75

The formula $C_{10}H_{14}O)_2.H_2S$ requires 89·82 per cent.

This formula was further confirmed by the estimation of sulphur, which gave 9·33 and 9·55 per cent. (calculated 9·59 per cent.).

On dilution with water after the boiling with hydroxylamine a bulky crystalline precipitate separated. This was collected, washed and recrystallised from hot alcohol. As thus obtained it melted at 216 to 218° C., whereas the oxime obtained in the same way from purified carvone melts at 71 to 72° C.

On analysis it gave:—Nitrogen 7·66 and sulphur 8·41 per cent. The formula $(C_{10}H_{14}NOH)_2.H_2S$ would require: Nitrogen 7·69 and sulphur 8·80 per cent.

CITRONELLAL.—The study of citronellal is complicated by the difficulty of preparing the substance in the pure state. We have succeeded in obtaining specimens which, when tested with hydroxylamine, gave a result of approximately 99 per cent., but the yield was very small, and the conditions difficult to reproduce, so that, as the main interest of the matter consists in the application of the method to citronella oil, it was considered best to work with a fairly pure sample (80 per cent.), testing this by the various methods and using it to make mixtures with geraniol and terpenes to correspond with the different types of citronella oil. (Cf. the Bulletins of Schimmel & Co., Oct. 1912, and of Roure Bertrand Fils, April, 1912 and 1913.)

The citronellal used gave by the hydroxylamine process the following results:— 80·85, 81·25, 81·60, 81·25, 81·0, and 80·10 per cent. of aldehyde. Average 81·0 per cent.

It was further analysed, as in the above-quoted papers, by acetylation before and after the conversion of the citronellal into its oxime, the difference between the two figures thus obtained representing the citronellal present. The acetylation was carried out by heating for two hours a mixture in the proportion of 10 grms. of acetic anhydride and 2 grms. of sodium acetate to 5 grms. of the citronellal.

By direct acetylation   104·0, 104·6, 98·3.   Average 102·3 per cent.
After oximation   24·1 and 22·1.   ,,   23·0   ,,
                 Citronellal by difference   ,,   79·0   ,,

The results are only moderately concordant, but the average corresponds fairly closely with that obtained by direct titration with hydroxylamine, and may be held to confirm the former result.

From this citronellal a mixture was prepared in the following proportions:— Citronellal, 49·85; geraniol, 40·05; and limonene, 10·10 per cent.

Calculating the citronellal used as containing 81 per cent. of the pure aldehyde, this mixture would contain 40·38 per cent. The total acetylisable constituents, calculated as geraniol, would be 89·90 per cent. The results were:—

Citronellal by hydroxylamine process, 40·6, 40·8, and 40·6 per cent.
Geraniol by phthalic anhydride method, 39·03 and 39·40 per cent.
"Total geraniol" by acetylation, 89·70 per cent.
Citronellal, by difference, after oximation, 39·65 per cent.

Further mixtures were prepared in which the proportions of geraniol and citronellal were varied, and the results of these, and of several commercial samples of citronella oil, are given in the following table:—

	Mixture I.	Mixture II.	Ceylon Oil.	Java Oil	Burma Oil
Citronellal-calculated	11·25	48·85	—	—	—
Citronellal by titration with hydroxylamine	11·40	48·50	8·55	32·05	40·35
Direct acetylation, "Total geraniol"	—	92·55	55·40	80·50	87·20
Acetylation after oximation	—	44·30	—	49·45	48·10
Difference-citronellal	—	48·25	—	31·05	39·10
Geraniol-calculated	43·00	30·25	—	—	—
Geraniol by phthalic anhydride method	42·90	—	29·60	46·75	35·10

By this method, therefore, the citronellal in a citronella oil is estimated by titration with hydroxylamine, and the geraniol by the phthalic anhydride method. The results are concordant among themselves and agree fairly with those obtained by the double acetylation, whilst the process is far more rapid and easy of execution, and much more economical in the reagents used.

CITRAL.—As it has been stated that the method, whilst giving satisfactory results for lemon essence, which contains only about five per cent. of the aldehyde, yields for the pure substance figures considerably below the theoretical, we add here a few results obtained with carefully purified citral:—

Taken Grm.	Found Grm.	Per Cent.
1·101	1·079	98·1
1·200	1·186	98·8
0·988	0·980	98·1
1·131	1·113	98·4

From this citral a mixture was made with geraniol, linalool and geranyl acetate to represent approximately the composition of a concentrated (sesquiterpeneless) lemon oil.

Weight of citral in mixture, 6·593 grms.   Calculated percentage of citral, 65·04.
Weight of alcohol and ester, 3·543 grms.   Found, 63·89 and 63·93.

If the citral is reckoned as containing actually 98·35 per cent. of the pure substance, the calculated percentage becomes 64·06.

The methods of analysis of such mixtures, depending on the absorption of the citral by sodium sulphite solution and measurement of the unabsorbed residue, are in many respects unsatisfactory.   Apart from the difficulty of reading the unabsorbed volume with any precision, and the probability of some mechanical loss (from droplets adhering to the side of the flask, etc.), geraniol and linalool are likely to be dissolved in appreciable quantities by the sulphite solution.   The fact of their complete absorption by dilute sodium bisuphite solution was pointed out by Dupont and Labaune (Bulletin of Roure Bertrand Fils, April, 1913).

The above mixture analysed by treatment with sodium sulphite solution, while neutralising from time to time with acetic acid the alkalinity produced, gave an absorption of 67·7 per cent., a result considerably above the truth.

We think therefore that the estimation of the aldehyde with hydroxylamine is greatly to be preferred in these cases.

DISCUSSION.

Mr. H. E. BURGESS said that the method appeared to be a very highly accurate one.   He had carried out similar experiments some years ago, but had used sodium bicarbonate instead of hydroxide.   As regards citronellal, he had found some samples to behave in the same way as the authors' samples, whilst others were very peculiar, and no matter what method was used, the figures obtained were very doubtful.   The results quoted in the paper spoke for themselves as being

accurate, but there were several objections to the method: (1) The reagent was very expensive; (2) It involved the use of a considerable amount of alcohol; (3) The length of time taken; and (4) It was doubtful whether it offered any advantage over the normal sulphite method. All the other substances spoken of by the authors gave equally good results with the sulphite method, the time taken was very small, and one could see what was going on. In commercial work the ordinary normal sulphite method was accurate enough. He considered that in reporting results mention should be made of the method employed.

Mr. CHASTON CHAPMAN said that, although he was not convinced that the hydroxylamine method presented in some cases any very great advantages over the sulphite method, he felt that the Society were very much indebted to the authors for this paper. Mr. Bennett's experience in this branch of chemical analysis was very great indeed; and whatever views they might ultimately be led to hold in regard to the value of the hydroxylamine method as compared with others, it was clear that the paper contained a record of a very great deal of painstaking and valuable work.

In regard to citronellal, it was well known that this underwent change with the production of isopulegol, and this was to some extent a disturbing factor in the case of those methods in which citronellal and geraniol were estimated together in terms of the latter. The authors' reference to a compound of carvoxime with hydrogen sulphide was interesting. A similar compound of carvone was well known, and, as carvoxime was an unsaturated compound, there did not appear to be any reason why hydrogen sulphide should not unite with it, assuming, of course, that that substance did not exert a reducing action. Hydrogen halides of carvoxime were known to exist.

Mr. NORMAN EVERS said he used brom-phenol blue in place of methyl orange, and in his experience found it to be much more satisfactory. The change from blue to yellow was very much sharper.

The Theobromine Content of Cacao-Beans and Cocoa.

By RAYMOND V. WADSWORTH.

(Read at the Meeting, March 1, 1922.)

ANYONE searching through the published figures for the theobromine content of the cacao-bean would be bewildered by the different results recorded. In the ordinary text-books on cocoa and chocolate there is little help, even in the latest editions. The following average percentages have been recorded by various authorities: 0·82 to 1·34 per cent. (Winton, Silverman and Bailey[12]); 1 per cent. (Knapp[24]); 1·4 to 1·80 per cent. (Parry[18]); 1·5 per cent. (Wynter Blyth[14]); 2 per cent. (British Pharmaceutical Codex[17]); 0·9 to 3·0 per cent. (Whymper[25]).

When one considers any individual cacao-bean, the range of recorded percentages is almost as wide, though one would expect a much smaller

variation.   Taking such beans as Trinidad and Caracas, the following results recorded by different workers, give an idea of the variations obtained :—

TRINIDAD NIB.

Moisture Per Cent.	Cacao butter Per Cent.	Theobromine Per Cent.	Authority
6·20	51·57	0·4	Zipperer[13]
6·34	43·66	0·85	Ridenour[7]
3·09	48·28	0·91	Winton, Silverman and Bailey[12]
5·62	45·71	1·05	Eastes and Terry[3]
		1·44	Maupy[10]
4·72	53·57	1·94	Eastes and Terry[3]

CARACAS NIB.

6·50	50·31	0·77	Zipperer[13]
5·13	51·45	1·03	Winton, Silverman and Bailey[12]
4·75	53·65	1·08	Eastes and Terry[3]
6·63	36·81	1·13	Ridenour[7]
		1·38	Maupy[10]
		1·43	Eminger[9]
		1·63	Wolfram[13]

It will be clearly seen from these figures that there is a need for either a revision of the percentages, or else some interpretation of the results—the latter never seems to have been attempted.

Many of the early workers obtained poor results simply on account of the methods then available for the estimation of theobromine, and it can be said that figures published before 1895—about which year both Eminger[9] and Kunze[6] published their methods—are of little more than historic value.   It is interesting to record one or two early figures, remembering that it was only in 1841 that Woskresensky isolated the alkaloid:—

	Bell[2] (1881) Per Cent.	Zipperer[4] (1886) Per Cent.	Eastes & Terry[3] (1885) Per Cent.
Guayaquil cacao	0·54	0·33	1·74
Grenada cacao	0·91		1·42
Surinam cacao	0·78	0·50	1·42
Trinidad cacao	0·59	0·40	1·05, 1·94

Although many workers obtained below one per cent., others recorded percentages up to 4 per cent.   (Payen[2].)

The author has, in a previous paper[26], criticised the present methods used for the estimation of theobromine, showing that not one of these would give accurate and concordant results.   Consequently, all the figures published contain some error and need revising.   To this task the present paper is intended as a contribution, and it is hoped that it may help to clear up the uncertainty, which so obviously exists, as to the amount of theobromine present in different cacao-beans, and provide an interpretation of the results obtained.

METHODS USED.—In a previous paper the author[26] has described a new method for the estimation of theobromine, depending upon the extraction of the alkaloid from the damp cacao mixed with magnesia, by means of tetrachlorethane, which gives accurate and concordant results.   This method has been used in all the work recorded below.

The method of procedure when examining cacao-beans was as follows:—The beans were carefully shelled by hand. The shell was ground to a powder, the particles of which were less than 0·04 inch, and immediately bottled for use. The nib was ground in a warm mortar until every particle was less than 0·005 inch. In the estimation of the fat a fine grinding is very necessary. After grinding, the liquid mass (which the ground nibs had become) was solidified by cooling. A portion of this was scraped finely with a knife, thus still further reducing the size of particles, and used for the estimation of the moisture and fat of the original nib. The remainder was roughly broken up and extracted for 24 hours in a Soxhlet with petroleum spirit (B.Pt. below 80° C.), which, it has previously been shown[24], does not dissolve the theobromine. The extracted mass was dried, thoroughly mixed and bottled ready for use. In dealing with such large quantities (60–100 grms.) it was found that after 24 hours' extraction, between 4 and 14 per cent. of fat was still left in the material; consequently the fat percentage and the moisture content had both to be estimated for the purpose of calculating the results back to the original nib.

When examining manufactured cocoas and shells the material could be used without any preliminary de-fatting being necessary.

In the case of nibs and cocoas the fat percentage varies very considerably with the different samples; thus the only method of comparison is between the results calculated on the dry, fat-free material. The results below are for this reason expressed on the dry, fat-free material as well as on the original cocoas. With shell, where the fat percentage is small and varies little, the figures are given on the dry shell as well as the original.

All the samples analysed were commercial samples obtained through the usual channels, and not special plantation preparations. Thus the results can be taken to represent the commercial cacao-bean at present coming on to the market.

THEOBROMINE PRESENT IN NIBS* OF DIFFERENT ORIGIN.—The order of arrangement in the following table is that of theobromine content on the dry, fat-free material, the nibs containing the highest percentage appearing at the top of the table. Under "remarks" are noted roughly the degree of fermentation and the colour of the cotyledons when cut through. These, it will be found, are the most important factors influencing the theobromine content of the bean. The terms "Forastero" and "Criollo" have been used in various ways. "Forastero" really means "foreign," whilst "Criollo" means "native." Thus, if this meaning is taken as a basis, the same kind of cacao would be Forastero to one man and Criollo to another, living, for instance, on a different island. The meaning, however, which it seems least confusing to accept, is that followed by van Hall[20]. He takes the Forastero cacao to be that which has a purple bean and is flattish, and the Criollo cacao to be that which has a whitish bean and is more plump. Both kinds, on fermentation, lose their original colours, but, whereas the Criollo becomes a beautiful light chocolate-brown, the Forastero becomes a deep black or purple-brown to very deep brown. Thus it is possible to distinguish by the

* Shelled Cacao-Beans.

colour of the bean the approximate type. It has not been found possible, as yet, to separate the different kinds of Forastero cacaos with accuracy; this is due to the shape and colour of the bean varying so much according to the length of fermentation, and to the various effects of the season, whether it be wet or dry. So, for the purpose of the following figures, the separation is only made into Forastero and Criollo:—

THEOBROMINE IN CACAO NIB.

(All from unroasted beans, *i.e.* cacao as marketed.)

Kind of beans	Moisture Per Cent.	Butter Per Cent.	Theobromine On original material Per Cent.	Theobromine On dry, fat-free substance Per Cent.	Remarks
Costa Rica (ordinary)	2·8	53·7	1·66	3·82	Very poorly fermented. Purple-brown.
Accra	2·7	52·7	1·69	3·80	All unfermented purple beans.
Costa Rica (fine)	3·18	56·4	1·53	3·77	Fermented. Purple to deep grey-brown.
	2·9	56·9	1·12	2·78	
Columbian	3·1	53·7	1·62	3·75	Very poorly fermented. Blackish-brown.
Lagos	2·7	53·0	1·56	3·51	Very poorly fermented. Blackish-brown.
San Domingo	2·9	52·2	1·51	3·36	Very poorly fermented. Purplish-brown.
Accra	1·6	53·3	1·52	3·38	Fermented. Purplish-brown.
	2·9	54·6	1·41	3·32	
	2·5	52 7	1·42	3·17	
Haiti	3·5	53·5	1·39	3·23	Poorly fermented. Blackish-brown.
San Thomé	2·7	54·8	1·36	3·20	Fermented. Purplish-brown.
Para	3·0	54·3	1·28	3·00	Poorly fermented. Blackish-brown.
Bahia	2·3	56·6	1·23	2·99	Fermented. Very deep brown.
Arriba	2·9	52·5	1·33	2·98	Poorly fermented. Deep browns and purples.
	2·8	52·0	1·32	2·93	
Caracas	2·5	52·7	1·32	2·95	Poorly fermented. Mixed. Mainly dark-brown.
Grenada	3·5	53·5	1·23	2·86	Fermented. Purple and browns.
Surinam	2·7	55 8	1·17	2·82	Fermented. Blackish-brown.
Cameroons	2·6	56·2	1·15	2·78	Highly fermented. Deep brown.
Machala	3·9	51·1	1·24	2·75	Poorly fermented. Deep brown and purple.
	2·9	51·8	1·40	3·09	
Trinidad	3·0	53·0	1·18	2·69	Fermented clayed beans. Deep browns and purples.
Ceylon	2·3	52·6	1·20	2·65	Fermented. Mixed browns and purples.
Jamaica	3·1	57·0	1·05	2·64	Fermented and unfermented. Mixed. Purples and browns.
	2·0	58·2	0·99	2·48	
Java	2·9	53·5	1·03	2·36	Poorly fermented. Washed. Light-brown to white.
Samoa	2·8	52·9	1·01	2·28	Light-brown beans.
Venezuela (clayed)	3·1	50·1	1·04	2·23	Do.
Do. (unclayed)	2·3	50·6	1·05	2·22	Do.

Expressed on the dry, fat-free material, it will be noticed that all the purple Forastero beans contain the highest percentage of theobromine, whilst all the light Criollo type of beans contain the lowest percentage. (H. C. Brill[22] found only a very slight difference in the theobromine content of Criollo and Forastero cacaos, and the latter, in his case, gave slightly the lower results.) From the figures given above there is no doubt that the light Criollo beans contain much less theobromine than the dark Forastero beans—a fact previously unrecognised.

There is also a distinct variation in the theobromine content of the nib of a particular bean; the three samples of Costa Rica vary by one per cent. and the Accra by 0·6 per cent. This difference is due, apart from the slight variation found in all natural products, to two causes:—*Firstly*: All the beans from one country are not of the same kind, the commercial samples being nearly always mixtures. If much cacao of the Criollo type is present, the alkaloid content is lowered, whilst if the whole is pure Forastero, it is raised. It is also highly probable that many trees now producing cacao are crosses between Criollo and Forastero, and this, for instance, is true of the Ceylon product. *Secondly*: The amount and type of fermentation influence the theobromine percentage considerably. From the table it will be seen that Accra unfermented cacao nib contains much more alkaloid than the fermented cacao nib. During fermentation theobromine is lost from the nib to a considerable extent. This conclusion is supported by other work of the author, in addition to that recorded here. It should be mentioned that Brill[22] says "during fermentation the theobromine shows no regular variation"; this is accounted for by the method used in the estimation, and it may be noted that his results are mainly very low. L. Nicholls[19] was also of the opinion that theobromine showed only a "very slight loss." Other authors even claim an increase.

The maximum variation found in cacao-beans of all types and grades is between 0·99 and 1·69 per cent. of theobromine on the original nib, and between 2·22 and 3·82 per cent. on the dry, fat-free material.

For the cacao-beans which form the bulk of the world's production the average percentage would be 1·2 to 1·7 per cent. of theobromine on the original nib, and 2·8 to 3·8 per cent. of theobromine on the dry, fat-free material.

THEOBROMINE PRESENT IN SHELLS OF DIFFERENT ORIGIN.—The number of figures published of the theobromine content of cacao-shell are small. The general percentages recorded are as follows:—0·2 to 0·90 per cent. (Winton, Silverman and Bailey[12]; 0·76 per cent. (Eminger[9]); 1 per cent. (British Pharmaceutical Codex[17]); 1·0 to 1·4 per cent. (Knapp[24]); 0·4 to 2·0 per cent. (Whymper[25]). It will be seen that Whymper gives a wider range than any other authority, and, although he quotes no figures to support this higher percentage, the table below shows that even this range does not include all commercial shells.

The table below gives the results the author has obtained on a number of different commercial cacao-shells:—

THEOBROMINE IN CACAO-BEAN SHELLS.

(Unroasted Beans.)

Shell from	Moisture Per Cent.	Theobromine On original material Per Cent.	On dry substance Per Cent.	Remarks.
Cameroons	12·3	2·61	2·98	Very loose shells. Very highly fermented.
Costa Rica (fine)	9·7	2·22	2·46	Well fermented.
	9·9	2·30	2·55	
Jamaica	12·5	2·15	2·46	Well fermented.
	14·0	2·00	2·33	
San Thomé	10·6	2·16	2·41	Weil fermented.
Bahia	12·6	2·08	2·38	Well fermented.
Surinam	11·5	1·96	2·22	Well fermented.
Accra	11·2	1·63	1·84	Well fermented.
	10·5	1·53	1·71	
Samoa	11·3	1·36	1·53	Brittle shell. Pure Criollo.
Grenada	11·5	1·16	1·31	Well fermented.
	10·2	2·07	2·30	
Java	11·8	1·10	1·25	Washed loose shells. Pure Criollo
Accra	10·6	0·98	1·10	Fermented.
Venezuela	10·0	0·87	0·97	Pure Criollo.
	8·7	0·77	0·84	
		0·85	0·93	
Trinidad	9·2	0·74	0·81	
		0·78	0·86	
Haiti	10·5	0·65	0·73	Poorly fermented.
Machala	13·0	0·52	0·60	Poorly fermented.
	10·1	0·47	0·52	
Costa Rica (ord.)	9·7	0·51	0·56	Poorly fermented.
Columbian	13·3	0·44	0·51	Poorly fermented.
Lagos	9·2	0·40	0·44	Poorly fermented.
Ceylon	13·5	0·38	0·44	Washed.
Arriba	8·4	0·42	0·46	Poorly fermented.
	13·6	0·37	0·43	
Caracas	9·6	0·36	0·40	Slightly fermented.
San Domingo	9·1	0·34	0·37	Slightly fermented.
Para	13·1	0·23	0·26	Slightly fermented.
Accra	10·5	0·17	0·19	All unfermented.

It will be noticed that there is no difference between shells from Criollo and Forastero beans, and that no interpretation of the results can be made from this point of view. The Criollo tends to take its place in the middle of the Forastero. It will, however, be easily seen that shells from unfermented cacaos are always low in theobromine, whilst those shells which come from well-fermented beans always contain a much higher percentage. Thus the medium fermented Criollo occupies a middle position. The original shell of the cacao-bean, fresh from the pod, contains only about 0·17 per cent. of theobromine (as will be seen from

the last figure in the table), and the alkaloid present in the shell is brought there by sweatings from the nib during fermentation. Thus the highly-fermented samples contain much more than do those which have been but poorly fermented.

This effect of fermentation has never previously been recognised. It helps us to understand the great variations which occur, and may help us to determine the approximate length of fermentation to which any particular sample has been subjected. When beans are very unevenly prepared, as in the case of the Accra cacao, it will be seen that the theobromine present in the shell varies very greatly (*e.g.* 0·19 to 1·84 per cent.); but where the bean is evenly prepared, the theobromine content is fairly constant, *e.g.* Trinidad cacao. If the bean is washed, as is so often the case in Ceylon, Java and Samoa, much of the alkaloid is washed away, and thus the fermentation of such beans cannot be judged in this way.

The maximum variation found in the shell of the cacao-bean of commerce is between 2·98 and 0·19 per cent. on the dry shell.

When shell is used for the commercial extraction of theobromine, it is obvious that well-fermented cacaos are to be desired.

THEOBROMINE PRESENT IN GERMS.—The germ is the radicle of the cacao-bean. So far as the author is aware, there is only one result published of the theobromine content of germs, that of Haussler[20], whose figures are as follows:— Fat, 7·8 per cent.; theobromine, 1·88 per cent.

The germs used in the analysis given below were separated commercially from a blend of roasted cacao-beans, and consequently do not represent the analysis of germs from one particular kind of beans. It must be said, however, that, although the author has analysed many samples from different blends, the results have been practically the same in every case. From this it appears probable that the variation in the theobromine content of the germs is small.

	Fat Per Cent.	Theobromine On original material Per Cent.	Theobromine On fat-free substance Per Cent.
Roasted cacao-bean germs	5·8	2·10	2·23

EFFECT OF ROASTING ON THE THEOBROMINE CONTENT OF NIB.—Most authorities are agreed that roasting of the cacao-bean has practically no effect on the theobromine content. The following are the results of the work of three authors on the subject:—

	Moisture Per Cent.	Butter Per Cent.	Theobromine Per Cent.
Weigman[5]			
Raw whole bean	7·93	45·57	1·49
Roasted whole bean	6·79	46·19	1·58
Zipperer[13]			
Raw shelled bean	7·11	51·78	0·45
Roasted shelled bean	6·71	49·24	0·43
Winton, Silverman and Bailey[12]			
Raw shelled bean	5·13	51·45	1·03
Roasted shelled bean, medium roast	3·71	51·65	1·02
,, ,, high roast	3·11	51·50	0·95

Whymper[25], however, disagrees with the above results, and gives the following figures which he obtained:—

	Theobromine Per Cent.
Raw bean	1·11
Roasted bean (120° C. 15 mins.)	0·77
,, ,, (230° C. 8 mins.)	0·25

The author's results, given below, support the figures, showing that there is practically no loss of theobromine during the roasting of the bean. Whymper's results must be due to the method employed for the estimation. Such a loss would mean that manufactured cocoas must contain very little alkaloid, which, in the latter part of the paper, will be seen not to be the case.

LOSS OF THEOBROMINE FROM NIB DURING ROASTING.

	UNROASTED.				ROASTED.			
			Theobromine					Theobromine
Nibs from	Moisture Per Cent.	Cacao butter Per Cent.	On original material Per Cent.	On dry, fat-free substance Per Cent.	Moisture Per Cent.	Cacao butter Per Cent.	On original material Per Cent.	On dry substance Per Cent.
Accra beans	2·9	54·6	1·41	3·32	2·1	54·8	1·47	3·42
	2·5	52·7	1·41	3·15	1·5	54·3	1·46	3·31
Arriba ,,	2·8	52·0	1·32	2·93	2·0	53·2	1·41	3·14
Machala ,,	2·9	51·8	1·40	3·09	1·6	52·9	1·37	3·00

EFFECT OF ROASTING ON THE THEOBROMINE CONTENT OF SHELL.—Very few figures are given for the loss of theobromine from shell on roasting. The figures quoted below are from Winton, Silverman and Bailey[12]:—

		Theobromine	
	Moisture Per Cent.	On original material Per Cent.	On dry, fat-free substance Per Cent.
Raw	8·69	0·33	0·36
Medium roast	6·01	0·48	0·51
High roast	5·16	0·56	0·59

It will be noticed that there is a slight increase during roasting. The author's results, given below, support this, so far as shells having a low theobromine percentage go. In the case of those shells which contain a high percentage there is a slight loss due to roasting. The shell comes into contact with the greatest heat, and with some type of roasting is liable to get slightly charred. It consequently follows that there would be a distinct loss of matter by volatilisation, and shells containing a high percentage of theobromine would lose the alkaloid on their surface readily.

LOSS OF THEOBROMINE FROM SHELL DURING ROASTING.

	UNROASTED.			ROASTED.		
		Theobromine			Theobromine	
Shell from	Moisture Per Cent.	On original material Per Cent.	On dry substance Per Cent.	Moisture Per Cent.	On original material Per Cent.	On dry substance Per Cent.
Accra beans	11·2	1·63	1·84	6·9	1·51	1·62
	10·5	1·53	1·71	5·0	1·61	1·69
Arriba beans	8·4	0·42	0·46	3·4	0·61	0·63
Grenada beans	10·2	2·07	2·30	5·0	2·1	2·21
Machala beans	10·1	0·47	0·52	3·3	0·55	0·57

THEOBROMINE CONTENT OF COMMERCIAL COCOAS.—Previous results published vary greatly, as in the case of the cacao-bean. The following is an average example:—

	Van Houten's Cocoa		
Moisture Per Cent.	Fat Per Cent.	Theobromine Per Cent.	Authority
4·53	29·78	0·69	F. Yaple[8]
	29·66	2·00	C. Girard[15]
		1·99–2·23	A. Kreutz[16]

From the results already given on cacao nibs it will be seen that the greatest bulk of cacao coming on the market (*i.e.* from the Gold Coast, Ecuador, San Thomé and Brazil) contains above 2·8 per cent. of theobromine, on dry, fat-free material. It follows that the majority of manufactured cocoas must generally contain a minimum of 3 per cent. (on the dry, fat-free substances) allowing for a blending of the different varieties. It will be seen from the following table that the analyses bear out this expectation:—

THEOBROMINE IN COCOAS.

Name of Maker and Country of manufacture	Name of cocoa	Moisture Per Cent.	Fat Per Cent.	Theobromine On original material Per Cent.	On dry, fat-free substance Per Cent.
Mazawattee (England)	Dee & Ess	6·9	31·7	2·18	3·55
Cailler (Switzerland)	Pure soluble	7·4	27·6	2·29	3·52
Van Houten & Zoon (Holland)	Rova	7·4	27·6	2·25	3·46
Cadbury (England)	Bournville	6·4	28·6	2·22	3·42
Fry (England)	Pure breakfast	4·1	28·0	2·32	3·42
Lipton (England)	Lipton's	5·9	25·0	2·35	3·40
Caley (England)	Fleur de Lys	6·1	32·8	2·05	3·36
Peradeniya Choc. Co. (Ceylon)	Peradeniya	4·9	40·5	1·81	3·32
Lyons (England)	Lyons'	4·5	25·2	2·32	3·30
Cadbury (England)	Essence	6·7	26·0	2·20	3·27
Bishop & Co. (America)	Bishop's	4·4	21·9	2·34	3·18
Rothwell (England)	Welco	7·3	23·3	2·20	3·17
Rowntree (England)	Elect	4·5	26·0	2·20	3·17
Armour (America)	Veribest	5·8	21·7	2·29	3·16
Horne & Sutton (England)	Digestive	6·3	26·6	2·12	3·16
Barber & Co. (England)	Essence	6·3	27·4	2·08	3·14
Peters (Switzerland)	Breakfast	5·9	20·5	2·25	3·06
Fry (England)	Concentrated	6·9	30·4	1·90	3·03
Watford Mfg. Co. (England)	Delecta	6·0	27·4	2·00	3·00
Co-op. Wholesale Sy. (England)	Essence	6·7	27·7	1·89	2·88
Caley (England)	Mella	4·6	31·1	1·62	2·52
W. Baker & Co. (Canada)	Breakfast	4·6	25·6	1·76	2·52
Van Houten & Zoon (Holland)	Pure soluble	6·0	25·0	1·65	2·39

CONCLUSIONS.—The theobromine content of the nib of the cacao-bean varies with the amount of fermentation to which the bean has been subjected, and also with the variety—Criollo or Forastero—to which it belongs. The maximum variation due to all these causes has been found to be between 0·9 and 1·7 per cent. on the original shelled cacao-bean, or between 2·2 and 3·9 per cent. on the dry, fat-free material. The lower limit represents the light Criollo bean, and the higher the dark, unfermented Forastero.

The variation of the theobromine percentage in the shells of the cacao-bean is much greater than in the nib, being between 0·19 and 2·98 per cent. on the dry shell, the lower figure here representing the unfermented cacao-shell, and the higher the shells from very thoroughly fermented cacaos.

The germ, as commercially separated from roasted cacao-beans, contains 2·1 per cent. of theobromine.

During roasting there is practically no loss of theobromine either from the nib or shell.

Manufactured cocoas of commerce contain a much higher percentage of theobromine than is usually accepted. It will be found that they generally contain between 2·0 and 2·3 per cent. of theobromine on the original cocoa, and between 3·0 and 3·6 per cent. on the dry, fat-free material.

The work was carried out in Messrs. Cadbury Bros. Research Laboratory, and the author wishes to thank the firm for their permission to publish these results.

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DISCUSSION.

Mr. A. W. KNAPP said that the point which specially interested him in the paper was the number of figures given by Mr. Wadsworth which proved that during fermentation the amount of theobromine in the nib decreased, because it appeared to be generally accepted by all save himself that during fermentation the amount of theobromine increased. This opinion had largely resulted from the theory that the bean, when taken from the pod, contained a glucoside which, during fermentation, split up into theobromine, dextrose and cacao-red. The glucoside theory was founded on very slender evidence, and Mr. Wadsworth's figures showed that it was in need of revision. The defence, which would be made by those who believed that the glucoside existed, would be that Mr. Wadsworth's process not only estimated the free theobromine, but also decomposed the glucoside and estimated the combined theobromine thus set free. Some analysts were so convinced of the presence of the glucoside, that they recommended that the cacao products should be treated with acid to hydrolyse it, before attempting to estimate the total theobromine. In Mr. Wadsworth's process treating with acid was unnecessary, which threw doubt on the glucoside theory. Another suggestion which had been made was that the theobromine originally existed in combination with tannin; such a compound would be readily decomposed by the magnesia used in Mr. Wadsworth's process. Mr. Wadsworth's figures showed that the theobromine found in cacao-shell came almost entirely from the interior, and this suggested a purely physical explanation of the distribution of the theobromine during fermentation. The bean, during fermentation, became permeated with liquid, and this distributed the theobromine evenly through the cotyledons and shell of the bean, and when the beans were subsequently dried, they dried naturally from the outside, with consequent concentration of theobromine in the shell. This would explain why, in a fully fermented bean, Mr. Wadsworth actually found more theobromine in the shell than in the nib. He thought Mr. Wadsworth's figures might help the botanist in the difficult matter of classifying the cacao from different countries. He noted that the author did not support Mr. Whymper's figures showing the loss of theobromine on roasting. The author actually obtained an increase, which he presumed proceeded entirely from the loss of volatile matter. The figures given in the paper for theobromine in cocoa were higher than those commonly accepted, and made one wonder why cocoa was not usually considered at least as stimulating as coffee.

Mr. CHASTON CHAPMAN asked whether the results given by the author related solely to theobromine, or included caffeine and any other bases that might be present in small quantity. If the numbers related to theobromine alone, he was rather surprised to see such high results.

Mr. CRIBB said that he had always felt considerable doubt whether cacao-shell really contained any alkaloid, and asked if Mr. Wadsworth considered the presence of theobromine in the shell from unroasted and unfermented beans as definitely proved. He also enquired whether the specimens of shell which yielded unusually low theobromine figures were derived from "earthed" beans.

Mr. WADSWORTH, referring to the question of the acid treatment giving a higher result than treatment by the ordinary method, said that estimations were made with an entirely unfermented bean, which would naturally contain the highest amount of glucoside; when examined without previous treatment the amount was 3·76 per cent. on the dry, fat-free material, when submitted to acid treatment it was 3·80 per cent.—a difference of 0·04 per cent. With "Arriba" beans the difference was:—Without acid, 3·0; with acid, 2·98 per cent. The figures obtained by his method represented the whole of the theobromine present, not only free theobromine, and did not represent the caffeine. Regarding the question of theobromine in unfermented shell, he had examined in England specially preserved unfermented beans direct from the plantation, and they always contained approximately 0·2 per cent. of theobromine. Time had, of course, elapsed in which changes might have occurred in the beans, but he thought that probably a small amount was always present. As to the earthing of beans, he considered it made very little difference in the percentage of theobromine. Heavily earthed beans contained, in the shell, 0·77 per cent., or 0·85 per cent. when corrected for the amount of earth.

The Value of Fish-Scales as a Means of Identification of the Fish used in Manufactured Products.

BY R. E. ESSERY, B.Sc., A.I.C.

IN the absence of facilities for the "precipitin" reaction it is often difficult or impossible to identify with any certainty the variety of fish present in a canned or potted fish product. This paper summarises some recent work, showing that in many cases valuable information may be obtained by a microscopical examination of the scales.

The majority of recent work on fish scales has had reference to the problem of age and growth determination only, and no published attempt has apparently been made to apply it to problems in the domain of food examination. Some references likely to be of use are appended.

Speaking generally, it may be said that the scales of a species are characteristic. This statement may be modified, however, by two considerations. Firstly, a whole genus, or perhaps several genera, may show scales so similar that it is difficult to distinguish them apart. Secondly, a fish may bear upon certain parts of its body scales abnormally marked and differing from type. Hence, scales alone are not sufficient to identify near species, but, even so, a microscopical examination will, in many cases, bring to light valuable information; and, by reference to the diagrams, it will be seen that, in certain cases, amongst well-known fish, typical scales are widely different in appearance, and are as characteristic as human finger-prints.
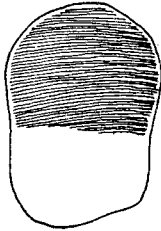
FISH-SCALES
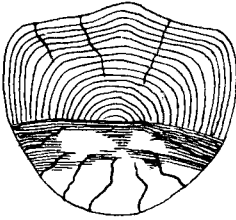
ANCHOVY
Engraulis encrasicholus
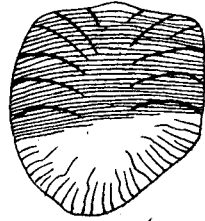
PILCHARD (Sardine)
Clupea pilchardus

HERRING
Clupea harengus

SPRAT (Brisling)
Clupea sprattus

SALMON
Salmo salar

COD
Gadus morrhua

HAKE
Merluccius vulgaris

It is recommended that permanent preparations of typical, known scales be made and used as standards for comparison.   These may be simply mounted dry, between two slides, or put up in glycerol jelly or Canada Balsam.   On removal from the fish, they may be cleaned, if necessary, by cautious warming with dilute sodium hydroxide solution, followed by thorough washing with water.   If required, the scales may readily be stained by the usual methods; but the author has found no practical advantage for the present purpose, either in staining or the use of polarised light.

In the examination of canned fish, all that is necessary is to remove some scales, and clean and examine them in water-mount.   It is well to note that the process of sterilising frequently renders the scales very brittle, and much care is needed in handling.   In view of the above-mentioned existence of abnormal scales, as many specimens as possible should be removed from the sample and compared with the standard slide.   A 2-inch power gives a satisfactory magnification.

When we come to consider fish-pastes, the problem becomes extremely difficult. The scales are broken up during the process of manufacture, and may lose their individuality more or less, in which case, it is generally not possible to obtain more than a clue to the nature of the fish present.   Close study of the fragments, and great caution in drawing deductions, are necessary.

The paste (about 10 grms.) may be mixed to a cream with aqueous sodium hydroxide solution (about N strength) and diluted to about 150 c.c., and the mixture gently warmed on a steam bath, with frequent stirring.   Under these conditions fragments of scales and bones sink to the bottom, while the rest of the material becomes flocculent, and can be decanted.   The scale fragments are then washed thoroughly by decantation, and examined in water.   Although, as a rule, reserve is necessary in reporting, in some cases the mere presence of bone and scale fragments is sufficient to indicate adulteration, as for instance their presence in lobster and shrimp pastes, where (these animals being crustaceans) their detection is clear evidence of admixture.   A 2-inch power is usually sufficient, any higher power being seldom required.

The drawings accompanying this paper are all to the same scale, namely, magnified about $3\frac{1}{2}$ diameters, and are diagrammatic, annual rings, etc., being omitted for the sake of clearness.   The fish were in most cases commercial specimens, but anchovy, sardine and sprat were kindly supplied by the British Museum. It may be remarked that cod belongs to a genus, other species of which are pollack, haddock and whiting, in which the various scales are so closely alike that they are difficult to distinguish.   Pilchard, also, should be noted in this respect, as the Indian sardine (*Clupea scombrina*), a relatively less valuable fish, bears scales practically identical in microscopical appearance with those of the pilchard.

In conclusion, the author wishes to express his thanks to Mr. A. E. Parkes, F.I.C., for continued interest and encouragement, and to Mr. C. T. Regan, F.R.S., of the British Museum, Dr. E. J. Allen, Marine Biological Association, and Mr. J. A. Hutton, for valuable information, and gifts of specimens and copies of papers.

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R. E. Savage: "Report on Age-Determination from Scales of Young Herrings." Ministry of Agriculture and Fisheries. Fishery Investigations, Series 2, Vol. IV., No. 1, 1919. (Photographs of herring scales.)

DISCUSSION.

Mr. A. E. PARKES pointed out that this paper involved a large amount of literary research, and was a valuable contribution to a hitherto unstudied subject. The method described would be found of value for the examination not only of fish pastes, but also of canned goods, such as sardines, anchovies and salmon, which frequently contained a fish of a different nature from that described on the label.

Mr. FINNEMORE enquired whether the writer of the paper had tried the clearing effect of a strong solution of chloral hydrate or sodium salicylate instead of sodium hydroxide.

Mr. C. L. CLAREMONT asked if the author had ever attempted to obtain a further differentiation by the use of polarised light.

Mr. ESSERY, replying, said that he had not tried the clearing effect of chloral hydrate. His first experiment had been with sodium hydroxide, and he had found it so effective that he had continued to use it. His method was to warm the sample with sodium hydroxide for about half an hour, when the protein and starchy matter could easily be decanted from the fragments of bone and scale. In reply to Mr. Claremont's question, he had tried the effect of polarised light, but in his experience it was so weak that it was hardly better than ordinary light. In some scales one gets bands, but the use of polarised light was of no advantage for the purpose under discussion.

Note.

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

A STARCH INDICATOR SOLUTION.

After considerable experimenting with starch solutions and pastes a method was devised for preparing a compound containing starch which is very stable and

not liable to decompose readily. The indicator was required to detect the presence of nitrites in water, for use in the Hübl and Wijs determinations, and to indicate the presence of free and combined iodine generally.

It was prepared as follows:— Common household (rice) starch was boiled with about an equal weight of sodium carbonate in solution, and the resulting mixture allowed to cool. Concentrated hydrochloric acid was then added until all action had ceased and the liquid was distinctly acid. Pieces of granulated zinc were then placed in the liquid, and it was allowed to stand for about 24 hours. It was filtered when neutral.

When prepared from pure materials the solution is perfectly clear and colourless, but in most cases impurities in the starch give the indicator a yellow tinge.

A solution prepared in this way on July 8th, 1921, still (March, 1922) gives a very distinct blue colour when tested in the following manner:—The starch solution (0·1 c.c.) is placed in Nessler cylinder and diluted to 100 c.c. with distilled water. The same quantity (0·1 c.c.) of a 0·1 N iodine solution is then added, and the solution stirred with a glass rod.

Mucilage of Starch B.P., prepared from the same starch, when tested in the above manner, gave no reaction after keeping for 10 days, whereas the other solution still reacts after keeping for over seven months.

3, NORTH STREET,   WILLIAM J. PAINTER.
    PLAISTOW, E.13.

Notes from the Reports of Public Analysts.

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

REPORT OF THE BIRMINGHAM PUBLIC ANALYST FOR THE FOURTH QUARTER, 1921.

During the quarter 1201 samples were analysed, of which 1029 were submitted under the Sale of Food and Drugs Act, and 163 were examined for various Corporation departments. Of the food and drugs samples, 816 were bought informally, and of these 43 were adulterated.

MILK.—The milk samples comprised 121 formal samples, 7 of which were adulterated, 390 informal samples (19 adulterated), and 78 of bottled milk (2 adulterated). The average composition of all the samples of milk was: Fat, 3·86; and solids not fat, 8·75 per cent. One sample contained 6 grains of boric acid per gallon.

CHICORY.—One of the 12 informal samples was adulterated, containing 8·3 per cent. of ash, of which 4·1 per cent. was sandy matter.

GROUND GINGER.—Nine of the 10 informal samples were genuine, but one contained 2 per cent. of powdered chalk.

SPONGE CAKE.—Eight samples were free, or practically free, from boric acid. The remaining 19 samples contained 0·15 to 0·84 per cent. and were condemned as adulterated. The ingredients used in making three of these samples, containing 0·48 to 0·51 per cent. of boric acid, were examined. The samples of flour, sugar and baking powder were free from boric acid, but the sample of liquid eggs contained 1·8 per cent. A circular letter was sent to the bakers and confectioners in the city calling their attention to the undesirability of using liquid eggs containing boric acid for preparation of cakes, etc.

CUSTARD POWDER.—Five of the 7 informal samples were of the usual composition, being coloured and flavoured starch. Two samples claimed to contain "24·37 per cent. of proteid," but the amount present was only 4·6 per cent. A letter of caution was sent to the vendor.

CITRIC ACID.—Sixteen samples were genuine and contained no excess of lead or arsenic. Two informal samples, and two formal samples, from two different vendors, consisted of tartaric acid. Each vendor was prosecuted and fined.

J. F. LIVERSEEGE.

DOMINION OF CANADA. DEPARTMENT OF AGRICULTURE.

INTERIM REPORT OF THE DOMINION CHEMIST.

FOR THE YEAR ENDING MARCH 31, 1921.

The report of the Dominion Chemist (Dr. F. T. Shutt, F.I.C.) includes agricultural investigation or research, chemical service for farmers, and chemical work for other Government Departments. During the year 3734 samples were received for analysis or examination.

INVESTIGATION WORK WITH FERTILISERS.—Experiments were carried out on 13 farms and experimental stations upon the influence of various fertiliser treatments on the development and yield of apple trees. Other questions studied were the effect of fertilisers, with and without lime, upon crops of potatoes, grain and clover hay; the influence of phosphoric acid in promoting maturity; and the influence of sodium nitrate on oat crops.

FERTILISING VALUE OF RAIN AND SNOW.—During the year 78 samples of rain and 29 of snow from the Ottawa district were analysed. The rainfall was 27·21 inches, which was slightly in excess of the average, and the snowfall was 66·9 inches (equivalent to 6·69 inches of rain), which was 27·3 inches less than the average for the previous 14 years. The total nitrogen ranged from 0·484 to 1·765 parts per million, the greater part of which was present in the form of free ammonia and nitrates. The total nitrogen was equivalent to 6·523 lbs. per acre, 4·874 lbs. of which were present as free and organic ammonia, and 1·649 lbs. as nitrates and nitrites.

LOSS ON SCOURING WOOL.—In all 102 samples were examined, the estimations of moisture being made by drying the wool for three hours at 100° C. The loss on scouring of various grades, as calculated on the "bone dry," greasy wool, ranged from 27 to 62 per cent., most of the results falling between 35 and 45 per cent.

SUGAR BEETS.—The systematic work on the quality of Canadian-grown sugar beets, and the influence thereon of soil and climatic conditions, has been continued at 18 experimental stations. Results obtained have shown that the sugar content and purity decline when the mean temperature for the season falls below 45° F.

FIELD ROOTS.—Analyses of mangels, turnips and carrots were made with the object of determining their relative feeding value, as indicated by (1) the percentage of dry matter, and (2) the percentage of sugar. The following results were obtained:—Mangels—dry matter, 12·40 to 6·64 per cent.; sugar in juice, 7·17 to 2·46 per cent.; turnips—dry matter, 14·00 to 10·09 per cent.; sugar in juice, 2·23 to 1·51 per cent. Carrots—dry matter, 11·22 to 7·53 per cent.; sugar in juice, 2·65 to 1·23 per cent.

DEVELOPMENT OF THE WHEAT KERNEL.—The kernels of two series of heads of Marquis wheat were analysed at eleven progressive stages of their growth. In both series the protein percentage (calculated on the dry matter basis) showed a

steady decrease from the first to the third cutting (July 21 to July 27), and then slowly increased to the end of experiment (August 15). The grms. of protein in 100 kernels

$$\frac{\text{per cent. protein} \times \text{weight of 1000 kernels}}{100}$$

was found to be a measure, at the dates specified, of the total weight of protein of the crop. This increased throughout the whole period, at first very rapidly, and, during the later stages of the ripening process, more slowly.

FEEDING STUFFS.—For some time past samples of bran have given results above the legal standard for protein (14 per cent.) and fat (not less than 3 per cent.), but higher in fibre (not to exceed 10 per cent.). This is due to more complete extraction of the floury particles in milling.

LIMESTONE.—Great variations were found in the quality of commercial ground limestones, some containing over 90 per cent. of calcium carbonate and others little more than 50 per cent. As regards fineness, a brand will usually be found satisfactory if from 65 to 85 per cent. passes an 80-mesh screen, all passing a 10-mesh screen.

MARL.—Three samples of air-dried marl from old lake bottoms in Eastern Canada gave the following results:—Mineral matter insoluble in acid, 20·48, 1·53 and 1·89 per cent.; iron oxide and alumina, 1·75, 0·48 and 0·61 per cent.; calcium carbonate, 66·10, 64·35 and 69·00 per cent.; and moisture, organic matter, etc., 11·67, 33·64 and 28·50 per cent. When of the best quality, marl gives results equal to those obtained with ground limestone.

MISCELLANEOUS FERTILISERS.—Samples of peat, tankage, blood and "sanding dust" were examined.

CUTTLE FISH BONE had the following composition:—Calcium carbonate, 89·30; insoluble mineral matter, 0·23; organic matter, 9·44; iron oxide and alumina, 0·33; phosphoric acid, traces; and undetermined, 0·70 per cent. Nitrogen in organic matter, 0·72 per cent. It would form an excellent poultry grit, and could be used for liming soils.

SAMPLES SUBMITTED BY HEALTH OF ANIMALS BRANCH.—The total number of samples examined was 1279, including 19 colours (now only used in jam factories); 449 samples of evaporated apples, 27 per cent. of which contained water in excess of the legal limit of 25 per cent.; 131 samples of spices and condiments; 84 samples of butter and oleomargarine, only 3·5 per cent. of which contained artificial colouring matter; and 39 of salts and preservatives.

Denaturing Oils.—To ensure that fats rendered from diseased carcases should not be used for edible purposes, department regulations require the addition of a denaturing agent to answer the following specifications : B. pt. not lower than 205° C.; flash point (open cup) not lower than 75° C.; taste easily recognised when added to fat in proportion of 0·1 per cent.; sp. gr. not lower than 0·819. Of the 63 samples examined only 27 per cent. answered all the requirements.

Meat and Vegetable Extracts.—Eight samples were examined. All were free from preservative, but one contained a large proportion of zinc, derived from the tank in which the extract had been stored. One product, imported in the form of cubes, contained about 50 per cent. of starch and 20 per cent. of salt.

Lard, Lard Compounds and Edible Oils.—In determining the purity of lard reliance has been placed upon the fact that beef fat, vegetable stearin and hydrogenated oils contain tristearin, which has not been found in lard.

Canned and Preserved Fruits.—Twenty-one of 85 samples contained commercial glucose (6·6 to 50 per cent.). Twenty-five contained artificial colour.

Sausages and Preserved Meats.—The average percentage of water in the 47 samples examined was 60·9 per cent., and the average percentage of cereal 6·22.

Fifteen samples contained cereal in excess of the permissible 10 per cent. (as starch). It is considered that this standard is unnecessarily high.

Canned Vegetables and Tomato Products.—The average amount of total solids in the 48 samples of tomato pastes was 30·8 per cent. One sample contained only 7·5 per cent. It is considered desirable that such products should be tested for the presence of moulds, bacteria and yeasts.

Condensed and Evaporated Milk.—All of the 204 samples examined were incubated for 10 days at 37°C. before analysis, as a test of their keeping qualities. All were in good condition after incubation, though some showed an excess of "sugar down" (i.e. deposition of lactose). Attention is directed to the frequent discrepancies between the weights stated on the tins and the actual net weights.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Zamia Starch. J. F. Clevenger. (*Amer. J. Pharm.*, 1922, **94**, 98–103.)— This starch is derived from the rhizomes of *Zamia floridana*, D.C., a diœcious plant belonging to the *Cycadaceæ*, found growing in a limited area near Miami, Florida. Analysis of the air-dried rhizomes yielded the following results:— Moisture, 7·73; ether extract, 0·63; protein ($N \times 6·25$), 6·17; crude fibre, 9·23; starch (diastase method), 37·75; ash, 5·01; and ash insoluble in 10 per cent. hydrochloric acid, 0·90 per cent. The starch is prepared by mixing the undried ground rhizome with water, passing the mixture through fine screens and running it into settling tanks, where a further separation of the starch from other vegetable tissues is achieved. After the starch has settled, it is dried, the whole operation occupying approximately three days. The water run off from the starch causes slow poisoning when consumed by animals, but the poison has not been identified. Microscopical examination of the starch shows that the majority of the starch grains are simple, with a small number of compound grains containing few components. The single grains are spherical, ovoid and dome-shaped, varying from 6 to 40 μ in length, with the majority ranging from 16 to 32 μ. This starch is placed on the market under the name of "Florida Arrowroot," and confusion is likely to result, since *Maranta arundinacea*, from which the true arrowroot starch is derived, is also grown in southern Florida.   T. J. W.

Influence of Dextrose on the Dialysis of Sucrose through a Parchment Membrane. L. A. Congdon and H. R. Ingersoll. (*J. Amer. Chem. Soc.*, 1921, **43**, 2588–2597).—The percentages of dextrose and sucrose dialysed in mixed solutions of the two sugars vary inversely as the concentrations. In cases where the concentration of the dextrose solution is not less than 2 per cent., and the time of dialysis more than two hours, the influence of the dextrose on the dialysis of sucrose in a mixed solution is of such a character as to keep the ratio of dextrose to sucrose constant, irrespective of the concentration of the sucrose. When the

solution contains less than 2 per cent. of dextrose, this sugar dialyses much more rapidly than does the sucrose, and in a 0·125 per cent. dextrose solution the rate of the percentage of dextrose dialysed to that of the sucrose is 5·0 to 1. In very dilute mixtures of dextrose and sucrose, the former can be separated from the latter in about fifty hours, and there is a possibility that the separation may be rendered quantitative.   W. P. S.

Formulae for the Direct Calculation of Starch Syrup and Sucrose in Fruit Juices, Jams, Etc. A. Rinck. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1921, **42**, 372–382).—Ten grms. of the sample are dissolved in water and diluted to 100 c.c. The total solids (T.S.) of this 10 per cent. solution are calculated from its specific gravity. Fifty c.c. of the solution are then inverted in the usual way, clarified with lead acetate, the mixture diluted to 100 c.c., and the polarisation determined in a 200 mm. tube; the reading is multiplied by 2 to obtain the polarisation (P) of the original solution. Then

$$\frac{T.S. \times 0·43 + P}{0·255} = \text{per cent. of anhydrous starch syrup in the sample,}$$

and $$\frac{T.S. \times 2·682 + P}{0·311} = \text{per cent. of sucrose.} \qquad \text{W. P. S.}$$

Sugar Content of the Hen's Egg. J. S. Hepburn and E. Q. St. John. (*J. Amer. Inst. Homeopathy*, 1921, **14**, 339–343; *Chem. Abstr.*, 1921, **15**, 3880).—The following amounts of dextrose were found in eggs analysed within six hours after being laid, each set of figures being based on the results obtained with six samples: Whole egg, 0·36 to 0·49, average 0·45 per cent.; white free from yolk, 0·29 to 0·57, average 0·44 per cent.; yolk free from white 0·11 to 0·15, average 0·14 per cent; yolks commercially separated 0·16 to 0·35, average 0·25 per cent. The results obtained with eggs which had been preserved for nine months in water-glass fell within the same limits, as did also those given by frozen whites. A sample of putrid white contained no dextrose.

Composition of Maize Oil. W. F. Baughman and G. S. Jamieson. (*J. Amer. Chem. Soc.*, 1921, **43**, 2696–2702.)—Maize oil was found to have the following composition, the figures representing percentages of the glycerides of the various fatty acids: Oleic acid, 45·4; linolic acid, 40·9; palmitic acid, 7·7; stearic acid, 3·5; arachidic acid, 0·4; lignoceric acid, 0·2; and unsaponifiable matter, 1·7 per cent.; total, 99·8 per cent. The unsaturated fatty acids were separated as bromides, and the saturated fatty acids by fractional distillation of their methyl esters. No hypogæic acid was present.   W. P. S.

Artificial Edible Fats. R. Escales and F. Schlesinger. (*Chem. Zeit.*, 1922, **46**, 157.)—During the war "ester margarine" was prepared in Germany by churning so-called "ester oil" (ethyl and glycol esters of fatty acids) with refined fat and milk. A new edible product has recently been made by esterifying stearic acid with isopropyl alcohol. The ester melts at 24° C., has a pleasant taste, and can be used as a main constituent of margarine.

Estimation of Glycerol in the Presence of Sugars. L. F. Hoyt and H. V. Pemberton. (*J. Ind. Eng. Chem.*, 1922, **14**, 54–56.)—Lævulose, dextrose and glycerol are quantitatively oxidised by treatment with excess of potassium dichromate and sulphuric acid. The following method for the estimation of sugar and glycerol in soap is based upon this observation: The soap (25 grms.) is dissolved in 300 c.c. of hot water, 50 c.c. of 25 per cent. sulphuric acid are added, and the mixture boiled gently for 30 minutes to eliminate alcohol and to invert the cane sugar present. After cooling, the cake of fatty acid is removed, and the aqueous solution transferred to a 1000 c.c. flask and treated with 0·5 grm. of silver sulphate, and the whole diluted to 1000 c.c., mixed and filtered. The invert sugar is estimated in 50 c.c. portions of the filtrate by the Munson-Walker method. Another 50 c.c. portion is treated with 75 c.c. of 7·455 per cent. potassium dichromate solution and 25 c.c. of concentrated sulphuric acid, and the mixture is covered with a watch-glass and heated for three hours in a steam bath. After cooling, the solution is diluted to 1000 c.c., and 50 c.c. portions are treated with an equal volume of water and 20 c.c. of 10 per cent. potassium iodide solution, and titrated with 0·1 N sodium thiosulphate solution. A blank estimation should also be made with 25 c.c. of the potassium dichromate solution, 25 c.c. of sulphuric acid and 100 c.c. of water. One cubic centimetre of the potassium dichromate solution oxidises 0·01 grm. of glycerol or 0·01142 grm. of invert sugar. The method yields consistent and accurate results, and may be applied to the estimation of glycerol and sucrose or invert sugar in fermented products, grape juice and non-alcoholic flavouring extracts, but is inapplicable in the presence of commercial glucose.

T. J. W.

Critical Solution Temperature of Oil of Lemon. G. Ajon. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 8–12.)—The author has determined the temperatures at which mixtures in equal volumes of alcohol of various concentrations and genuine or adulterated oils of lemon become homogeneous. The determination of this critical solution temperature is one of extreme sensitiveness, and should always be effected under the same experimental conditions, and great care is necessary in reading both the volumes of the liquids and the temperatures. The solubility of an oil of lemon in alcohol, and therefore its critical solution temperature, is related intimately to the density of the alcohol employed. Alcohol of higher density is most suitable for rendering evident adulteration of oil of lemon with terpenes, such adulterated oils showing very high critical solution temperatures. The final fractions of an oil of lemon, containing increased proportions of oxygenated compounds, exhibit high solubilities in alcohol and consequently low critical temperatures. Removal of citral from either natural or distilled oil of lemon raises the critical solution temperature. In order to apply such results to the detection of adulteration of oil of lemon with terpenes, an alcohol of suitable density must be chosen, and the limits ascertained between which this temperature varies for oils of different origins and ages. T. H. P.

Estimation of Caffeine by Means of Silicotungstic Acid. A. Azadian. (*Bull. Soc. Chim. Belg.*, 1922, **31**, 15–18.)—In the presence of about 5 per cent. of

hydrochloric acid caffeine is precipitated quantitatively by silicotungstic acid; when dried at 30° C. the composition of the precipitate is $12WO_3.SiO_2.2H_2O.$ $3(C_8H_{10}N_4O_2) + 6H_2O.$ On calcination this leaves $12WO_3.SiO_2$, which, multiplied by 0·2646, gives the equivalent of caffeine. The following method is suitable for the estimation of caffeine in tea, coffee and preparations of kola: Five to 10 grms. of ground tea or kola are boiled under a reflux condenser for two hours with 225 c.c. of water and 2 grms. of basic lead acetate; the liquid is filtered, the lead removed by means of hydrogen sulphide, and the filtrate evaporated to about 100 c.c. Hydrochloric acid is added, then excess of a 5 per cent. aqueous solution of silicotungstic acid, and the mixture boiled and set aside for 24 hours. The precipitate is filtered off, washed with water till free from acid, and ignited. Tincture or extract of kola is evaporated to a syrup on the water bath, diluted, filtered, acidified, and the caffeine precipitated as above. H. E. C.

Estimation of Monobrom-Camphor. E. O. Eaton. (*J. Ind. Eng. Chem.*, 1922, **14**, 24.)—A weighed quantity of the powdered sample containing approximately 0·2 grm. of monobrom-camphor is treated with 25 c.c. of alcohol, the mixture being warmed and filtered. The residue is washed with more alcohol, and to the combined filtrate and washings are added 50 c.c. of 0·5 N alcoholic potassium hydroxide solution and 25 c.c. of alcoholic silver nitrate solution containing 0·1 grm. of the salt. The mixture is boiled gently under a reflux condenser for ninety minutes, during which period further small quantities of the alcoholic silver nitrate solution, totalling 25 c.c., are added at intervals. After cooling, the contents of the flask are transferred to a porcelain basin, diluted to 200 c.c. by the addition of water and decanted into a beaker, and the residual silver oxide washed by decantation with water. The aqueous-alcoholic solution is boiled with 1 grm. of zinc dust for five minutes, filtered and treated with dilute nitric acid and aqueous silver nitrate solution, and the weight of precipitated silver bromide estimated in the usual manner. This weight, multiplied by 1·23, gives the quantity of monobrom-camphor originally present. Tabulated results given in the original paper indicate a possible maximum error of 4 per cent. T. J. W.

Bacteriological, Physiological, etc.

Castor Bean Lipase. Its Preparation and some of its Properties. D. E. Haley and J. F. Lyman. (*J. Amer. Chem. Soc.*, 1921, **43**, 2664-2670.)— A material containing lipase and free from fat may be obtained by grinding decorticated castor oil beans and extracting the powder with petroleum spirit in a Soxhlet apparatus. The extracted material is then passed through a 40-mesh sieve. The lipase zymogen of castor oil beans is somewhat soluble in fats and in a mixture of fat and ethyl ether; it is insoluble in the latter in the absence of fats. Lipase zymogen is activated by acid, but, in the absence of fats, the enzyme is unstable and is destroyed rapidly. The optimum hydrogen ion concentration for lipase activity is about 1×10^{-5}. W. P. S.

Preparation of Creatinine from Meat Extract. **H. Stendel.** (*Zeitsch. Physiol. Chem.*, 1921, **112**, 53–54; *Chem: Abstr.*, 1921, **15**, 2891.)—Creatinine may be obtained in pure condition by treating Liebig's extract with two successive portions of twice its weight of hot absolute alcohol, and distilling the clear supernatant liquid until of the consistence of a syrup. The creatinine, which crystallises from the concentrated alcoholic extract, is recrystallised from water, without using animal charcoal. One kilo. of meat extract yields 30 grms. of air-dried creatinine.

Quantitative Estimation of the Duration of Caffeine Excretion in Man. **E. Friedberg.** (*Biochem. Zeitsch.*, 1921, **118**, 164–184; *Chem. Abstr.*, 1921, **15**, 2891–2892.)—The urine under examination is treated with a few drops of a 5 per cent. solution of sodium carbonate, and evaporated on the water bath with dry calcium sulphate, and the residue dried *in vacuo* over sulphuric acid, finely pulverised, and extracted with 20 c.c. of petroleum spirit (b.pt. 50°–80° C.) beneath a reflux condenser. The solvent is removed by means of suction and replaced by 20 c.c. of anhydrous chloroform, and the extraction continued for an hour. The chloroform extract of the caffeine is dried with 1 grm. of anhydrous sodium sulphate, cooled, filtered and distilled. The residue is dissolved in 0·25 to 2 c.c. of Ringer solution and its caffeine content estimated by tests applied to muscle fibres from the sartorius of the frog. The fibre is treated with 0·1 c.c. of the solution, the degree of contraction noted under the microscope, and the extract continually diluted until the limit of the reaction is reached. The amount of extract obtained from the urine multiplied by the dilution, divided by 3500, gives the amount of caffeine excreted. The method is capable of detecting 0·00007 grm. of caffeine, with a possible error of about 10 per cent. Ten mgrms. of caffeine is the smallest amount of the pure alkaloid which, when given by the mouth, yields a positive reaction in the urine. Relatively small quantities of coffee cause the urine to give the reaction. When tobacco containing caffeine is smoked, the drug is absorbed. The excretion of ingested caffeine decreases somewhat rapidly, probably owing to transformation of the alkaloid into methylxanthine in the organism. Increased destruction of caffeine on continued ingestion does not occur. It should be noted that methylxanthine may be present in the urine and give the reaction.

Influence of Peptone on the Formation of Indol by B. Coli. **F. W. Tilley.** (*Amer. J. Pub. Health*, 1921, **11**, 834–836; *Chem. Abstr.*, 1921, **15**, 3505.)—A typical strain of *B. coli* will give a negative, weak, or strong indol reaction according to the composition of the peptone used. Each fresh supply of peptone should therefore be tested as to its suitability for the test, and to determine its optimum time for the incubation. The relative value of peptones for use in the indol test may be ascertained by testing them for the presence of tryptophan.

Pectinase Produced by Different Species of Rhizopus. **L. L. Harter and J. L. Weimer.** (*J. Agric. Research*, 1921, **22**, 371–377.)—All of the eleven species of *Rhizopus* studied were found to secrete pectinase, the amount produced varying

with the species. In each case some of the enzyme diffused into the surrounding culture solution. Two species, *nigricans* and *artocarpi*, both of which are parasitic on the sweet potato, secrete a relatively small amount of pectinase. On the other hand, two non-parasitic species, while retaining a small amount of enzyme in the mycelium, excrete a relatively large amount into the culture medium.

Chemical Changes involved during Infection and Decay of Wood and Wood Pulp. M. W. Bray and J. A. Staidl. (*J. Ind. Eng. Chem.*, 1922, **14**, 35–40.)—Examination of sound spruce wood and similar material in various stages of decay by the methods employed by Schorger (ANALYST, 1917, **42**, 336–338), in addition to estimations of lignin, and determination of the solubility in 7·14 per cent. sodium hydroxide solution and the "copper number" (reducing power), has led to the following conclusions:—As decay proceeds, the stable α-cellulose is converted into the unstable β- and γ- celluloses, the substances soluble in cold and hot water and in sodium hydroxide solutions increase in amount, and the "copper number" shows a large increase, indicating the development of reducing substances. Evidence was obtained of a decrease in pentosans and an increase of methylpentosans, but the experimental results were subject to numerous errors. No changes were observed in the ether-soluble material, ash, or in the amount of lignin present during the early stages, but in extreme decay the degradation of cellulose and lignin is selective and not uniform. The effect of these changes upon the manufacture and yield of sulphite, soda and ground wood pulps is discussed in the original paper. T. J. W.

Allyl Alcohol as a Preservative for Blood. E. Salkowski. (*Biochem. Zeitsch.*, 1921, **118**, 244–257; *Chem. Abstr.*, 1921, **15**, 2891.)—The addition of 0·5 to 0·6 per cent. of allyl alcohol will prevent blood from putrefying for five or six days. Its advantages as a preservative are that it is miscible with water, that it causes no change in the blood, and that it can be completely removed when the blood is dried to a powder.

Solubility of Carbon Monoxide in Serum and Plasma. H. R. O'Brien and W. L. Parker. (*J. Biol. Chem.*, 1922, **50**, 289–300.)—The solubility was investigated by bubbling carbon monoxide through serum or plasma at atmospheric pressure and at definite temperatures from 15°–37° C. The gases were removed from the solution by means of a mercury pump and analysed, the carbon monoxide being absorbed in ammoniacal cuprous chloride. Estimations were made with ox, sheep and human sera and ox plasma, each at five different temperatures, and the same results were obtained with all the liquids. Comparison with the solubilities of carbon monoxide in distilled water showed that in serum the volume of the gas dissolved amounted to 80 per cent. at 15° C., and 72 per cent. at 37° C. Experiments made with air containing 1·13 per cent. and 9·8 per cent. of carbon monoxide indicated that the laws of partial pressure were valid when using serum and plasma, and no accuracy would be gained in the investigation of ordinary cases of poisoning by making an allowance for carbon monoxide dissolved in the serum. T. J. W.

Modification of Folin's Colorimetric Method for the Estimation of Uric Acid. H. Jackson and W. W. Palmer. (*J. Biol. Chem.*, 1922, **50**, 89–101.)—Two disadvantages of Folin and Wu's method (*J. Biol. Chem.*, 1919, **38**, 8, 450) are the liability of the final colorimetric solution to precipitate, and the faintness of the colour produced. These difficulties are overcome by substituting sodium cyanide for sodium carbonate as an alkalising agent, the use of a standard uric acid solution not containing sulphite, and a phosphotungstic acid solution consisting of a mixture of solutions of "Phosphotungstate B" and "Phosphotungstate D" both of which are prepared from Folin's reagent by different methods. For details of procedure the original paper should be consulted. The colour developed by this modification is almost five times as intense as that given by the original method, and does not fade during a period of several hours. The results obtained are practically identical with those given by Folin's method.   T. J. W.

Colorimetric Estimation of Minute Amounts of Uric Acid. J. L. Morris and A. J. Macleod. (*J. Biol. Chem.*, 1922, **50**, 55–63.)—The arseno-18-tungstic acid solution used is prepared by boiling 100 grms. of hydrated sodium tungstate, 125 grms. of arsenic anhydride and 650 c.c. of water for about three hours. If the solution shows a blue or green colour, it should be decolorised by boiling with bromine water until all free bromine is expelled, after which the solution is diluted to one litre. One c.c. of urine is diluted to about 40 c.c., 1 c.c. of 2·5 per cent. zinc chloride solution added, and the mixture stirred, after which 1 c.c. of 10 per cent. sodium carbonate solution is run in, and the mixture is again stirred and centrifuged, the clear solution being discarded. The precipitate is dissolved in a few drops of 10 per cent. hydrochloric acid, diluted with 5 c.c. of water, 10 c.c. of 10 per cent. sodium cyanide solution are added, and the mixture is transferred to a graduated 100 c.c. flask and diluted to about 60 c.c. A standard for comparison is prepared by running 2 c.c. of the Benedict-Hitchcock phosphate solution (*J. Biol. Chem.*, 1915, **20**, 619) into a graduated 100 c.c. flask, diluting it to 60 c.c., and adding 10 c.c. of the sodium cyanide solution. To each flask are added 2 c.c. of the arseno-tungstic acid reagent, and the contents are diluted to the mark, well mixed, and allowed to stand for a few minutes, and the intensity of the colours compared in a colorimeter. By slight modifications this method is applicable to the estimation of uric acid in blood. The results obtained are generally intermediate between those given by the Benedict-Hitchcock method and by the Folin-Wu method (*J. Biol. Chem.*, 1919, **38**, 81, 459).   T. J. W.

Agricultural Analysis

Relation between the Chlorine Index and the Nitrogen Content of Vegetable Mould. C. Veil. (*Compt. Rend.*, 1922, **174**, 317–319.)—A relationship exists between the volume of chlorine absorbed from sodium hypochlorite and the nitrogen content of soils taken from five districts in France. The estimation of the chlorine absorbed is carried out by Lapicque and Barbe's method (ANALYST, 1919, **44**, 101) upon 10 c.c. of moist soil, which is found to weigh 15 grms. in most

cases (rather less in the case of soils rich in organic matter, and rather more in the case of soils rich in quartz). The chlorine index is expressed by the volume ratio $\frac{\text{chlorine}}{\text{soil}}$ in c.c. on the moist soil, and the nitrogen by weight in the dry soil. With the richest soils the nitrogen is greater than 4 per 1000, and the chlorine index greater than 30. Soils low in humus, with nitrogen less than 1 per 1000, give a chlorine index between 7 and 12, and soils with chlorine index between 15 and 27 have a content of nitrogen between 1 and 2 per 1000.   H. E. C.

Organic Analysis.

Methods for the Identification of Thymine. T. B. Johnson and O. Baudisch. (*J. Amer. Chem. Soc.*, 1921, **43**, 2670–2674.)—Of the three pyrimidines resulting from the hydrolysis of nucleic acid, two (uracil and cytosine) may be identified by the formation of the purple-coloured barium salt of dialuric acid when their aqueous solution is oxidised with bromine and then treated with barium hydroxide; this reaction is not given by thymine. If, however, the three substances are treated with ferrous sulphate solution and an excess of sodium hydrogen carbonate, and the mixture is aerated thoroughly, the thymine molecule is destroyed, with cleavage of the pyrimidine ring and formation of pyruvic acid, acetol, urea and formic acid; pyruvic acid and acetol are normal products of the oxidation of thymine, but not of uracil and cytosine. Pyruvic acid may be identified by the formation of indigo when it is treated in alkaline solution with *o*-nitrobenzaldehyde. To detect the acetol, the solution is distilled, the distillate is treated with a few drops of *o*-aminobenzaldehyde, the mixture rendered alkaline with potassium hydroxide and boiled; after cooling, the solution is acidified with dilute hydrochloric acid and then rendered alkaline with sodium hydrogen carbonate A blue fluorescence develops as the result of the formation of 3-oxyquinaldine. The latter may be obtained as nearly colourless crystals by extracting the mixture with ether and evaporating the ethereal solution. An alcoholic solution of 3-oxyquinaldine, when diluted with water, yields a deep blue fluorescence, and gives a deep red coloration when treated with alcoholic ferric chloride solution.
W. P. S.

Aleppo Oil of Turpentine. G. Dupont. (*Comptes rend.*, 1922, **174**, 395–398.)—Fresh Aleppo oil of turpentine contained 95 per cent. of *d*-pinene, 1·14 per cent. of inactive bornyl acetate and 3·8 per cent. of a sesquiterpene, with b.pt. 253–254°, sp. gr. 0·9096 at 15° C. and 0·9056 at 20° C., n_D^{20}, 1·4977°, resembling caryophyllene, but yielding a nitrosite with m. pt. 148–149° C.   T. H. P.

Estimation of the Acid Value of Tung Oil and Other Vegetable Oils. L. L. Steele and G. G. Sward. (*J. Ind. Eng. Chem.*, 1922, **14**, 57–58.)—The use of a mixture of equal parts of alcohol and benzene as solvent for the oil in the estimation of the acid value gives results both higher and nearer to the theoretical values than when alcohol alone is employed. With tung oil the increase is approximately 0·5, but with linseed and cottonseed oil the increment is less;

whilst the fatty acids of these oils and rosin show no difference whichever solvent is used. The oils under examination are readily soluble in the alcohol-benzene mixture, and a much sharper end-point is obtained by the use of this solvent. No difference is observed whether aqueous or alcoholic alkali is used for titration when not more than 15 c.c. are added to approximately 50 c.c. of the oil solution, but in the case of substances with high acid value alcoholic alkali is recommended in order to avoid hydrolysis. T. J. W.

Estimation of Moisture in Insulating Oils. C. J. Rodman. (*J. Ind. Eng. Chem.*, 1921, **13**, 1149–1150.)—From 25 to 40 c.c. of the oil are placed in a bulb or round-bottomed flask which is fitted in a mechanical shaker; the bulb is connected by a length of rubber pressure tubing with a *U*-tube cooled by a mixture of solid carbon dioxide and acetone or by liquid air, and the *U*-tube in turn is connected with a weighed vessel containing phosphorus pentoxide. The air is exhausted from the whole apparatus and the oil in the bulb is heated gradually

to 140° C. and shaken. The water vapour is eliminated rapidly from the oil and is frozen in the *U*-tube, which also condenses any light oil distillate. On removing the freezing mixture, the water evaporates and is absorbed by the phosphorus pentoxide; the latter does not absorb any oil vapour at the pressure used (about 1 mm.). Allowance may be made for the moisture contained in the air in the apparatus. W. P. S.
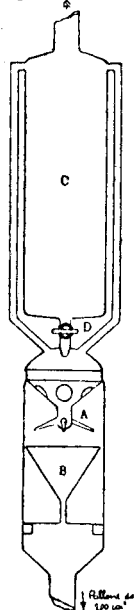
New Apparatus for the Estimation of Impurities in Fats. Somazzi. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 25–26.)—The central part of this apparatus contains a funnel B provided with a foot and is closed above by means of a condenser C, beneath which is the distributor A. The apparatus is fitted to an ordinary flask. The substance to be examined is weighed in the funnel B, which is then introduced into the apparatus. When the solvent in the flask is boiled the condensed liquid falls into the funnel and removes all the fatty matters. Towards the end of the operation the tap D is closed, the solvent then collecting in C being used for a thorough washing of the funnel. The funnel is finally removed, dried at 100° C. and weighed. It is suggested that this method be adopted officially. T. H. P.

Rapid Estimation of the Weighting of Silk. C. Tondani. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 17.)—Weighting of silk by means of tin, bismuth, tungsten, lead and barium salts may be estimated rapidly by means of X-rays, the negatives obtained being compared with a series of negatives furnished by similar fabrics weighted to varying and known extents. Silk weighted with tanning materials or Prussian blue gives indefinite results by this method. T. H. P.

Identification of Wood Extract by Means of Cinchonine. L. de Hesselle. (*Collegium*, 1921, 425; *J. Soc. Leather Trades Chem.*, 1922, **6**, 73.)—When tested by the method of Appelius and Schmidt, some synthetic tannins are not precipitated, whereas others give a precipitate similar to that given by wood extract. In the author's modified method of identifying wood extract, 100 c.c. of the solution of the usual strength for analysis are boiled for two minutes with 5 c.c. of 40 per cent. hydrochloric acid, cooled and filtered. Fifty c.c. of the clear filtrate are treated with 10 c.c. of pure tannin solution (15 grms. per litre) and 10 c.c. of cinchonine solution (15 grms. per litre, with sufficient sulphuric acid to make the solution clear). The whole is slowly boiled, when, in the presence of wood extract, the characteristic brown black precipitate will be formed. For a quantitative estimation of wood extract 7·5 grms. of the sample are dissolved in 450 c.c. of water, 25 c.c. of the acid are added, and the mixture made up to 500 c.c. One hundred c.c. of this solution are boiled for two minutes, cooled, made up to 100 c.c. again, and filtered, 50 c.c. of the filtrate are mixed with 10 c.c. of the tannin solution and 10 c.c. of the cinchonine solution, and the whole heated to boiling. The precipitate is filtered off, washed for two to three hours with boiling water, dried, and weighed.

R. F. I.

Indirect Determination of the Calorific Value of Fuel Naphtha. G. Morpurgo. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 15–17.)—The examination of liquid fuels should include determinations of the specific gravity at 15° C., the viscosity at 50° C. and 100° C., the flash point and the proportions of coke, ash, sulphur and moisture, besides fractional distillation up to 310° C. The moisture is deduced from the amount of water separating during the distillation. The coke is estimated as follows: Five grms. of alumina are heated to constant weight in a covered crucible, 2 or 3 grms. of the oil and a layer of the heated alumina being then added and the weight again taken. The crucible is next heated gradually to about 350° C., until evolution of vapour ceases, and is then covered and heated to redness until of constant weight; the weight thus found is diminished by that of the ash to deduce the fixed carbon. The sulphur is estimated by treating a few grms. of the fuel repeatedly with nitric acid on the water-bath, the residue being mixed to a paste with saturated potassium hydroxide solution, and finally heated to obtain a dense, viscous mass, to which is added sufficient magnesium oxide to yield a friable material. This is placed in a crucible, covered with a layer of sodium carbonate, and heated for an hour to about 300° C. and then to dull redness. The residue is pulped with water, treated with sufficient bromine water to give a faint yellow coloration, heated on a water-bath and acidified with hydrochloric acid, the sulphate being determined in the filtered solution.

The fractional distillation is carried out in an ordinary Engler flask on 50 grms. of the oil. The fractions below 110° C. represent hydrocarbons of the nature of benzine (*a*), with a calorific value of 11,200 cals., those between 110° and 310° C. petroleum (*b*) with the mean calorific value 10,300 cals., and those above 310° C. dense oils (*d*) with the calorific value 10,000 cals. The calorific value of the fixed

carbon (c) is 8,140 and that of the sulphur (z) 2,500 cals. The water present does not pass into the fuel injector, and thus, like the ash, acts merely as a diluent. Thus, the calorific value of a liquid fuel may be calculated by means of the formula:

$$\frac{11200\,a + 10300\,b + 10000\,d + 8140\,c + 2500\,z}{100}.$$ T. H. P.

Ultimate Composition of British Coals. **T. J. Drakeley and F. W. Smith.** (*J. Chem. Soc.*, 1922, **121**, 221–238.)—The composition of coals, in terms of carbon, hydrogen and oxygen, is represented graphically on the triangular co-ordinate system (*cf.* Ralston, abst., *J. Soc. Chem. Ind.*, 1916, **35**, 955). LMN is an isoceles triangle, right angled at L, the percentage of carbon and hydrogen is represented by the distances from the vertical LM and the base LN respectively, and the oxygen by the distance from the hypotenuse MN. It is found that all classes of coal from lignite to anthracite, when so plotted, lie in a narrow continuous band in the angle MNL, with the exception of cannels, which are essentially different from ordinary coals. The different classes of coal fall into well-defined areas in this band, and lines may be drawn showing the variation in fixed-carbon content, coking, and other properties of the coals, even distinguishing between different types of coal which happen to have nearly the same ultimate analysis. The bearing of the results on the constitution of coal is discussed. The radium content of some coals was estimated by ashing 40 grms., dissolving the ash in hydrochloric and hydrofluoric acids, and evaluating the radium content with an emanation electroscope. The following results were obtained:—

Coal Field Class	Leicestershire Non-coking	Derbyshire Non-coking	Lancashire Cannel	Lancashire Cannel	South Wales Anthracite
Carbon, per cent.	76·44	78·48	79·55	82·07	88·41
Hydrogen	4·90	5·71	5·81	6·15	3·41
Nitrogen	1·53	0·93	1·19	1·54	1·04
Sulphur	0·83	0·79	0·96	1·48	1·27
Ash	2·52	1·38	5·17	2·38	3·85
Oxygen	13·78	12·71	7·32	6·38	2·02
Total	100·00	100·00	100·00	100·00	100·00
Radium per grm. of ash $\times 10^{12}$	2·66	3·91	1·28	0·042	0·78
Radium per grm. of coal $\times 10^{12}$	0·067	0·054	0·066	0·001	0·030

H. E. C.

Agglutinating Value of some Durham Coals. **A. Weighell.** (*J. Soc. Chem. Ind.*, 1922, **41**, 17T.)—Samples of coal from the western margin of the Durham Coalfield were ground to pass 1/60 sieve, mixed with electrode carbon graded 1/100 to 1/120, and the agglutinating value determined. (*Cf.* Sinnatt and Grounds, *J. Soc. Chem. Ind.*, 1920, 83T.) One grm. is heated in a closed

crucible over a Bunsen burner for seven minutes with such proportion of carbon that the button of coke just falls to powder when a 100 grm. weight is laid upon it. The following values were obtained for different pits in the various seams:— Brockwell Seam, 17·0 to 8·0; Three-quarter Seam, 21·0 to 10·5; Busty Seam, 19·0 to 6·0; Five-quarter (Bottom Busty) Seam, 17·0 to 10·5; Stone Coal (Top Busty), 16·5 to 10·0; Tilley Seam, 15·5; Towneley Seam, 13·5, 12·5; Thick Seam, 15·5; Main Seam, 14·0; Little Seam, 15·0; Hutton Seam, 15·0 to 13·5; Ruler Seam, 18·5; Shield Row Seam, 16·5 to 4·6.   H. E. C.

Inorganic Analysis

Sodium Hydrosulphite.   F. W. Heyl and F. E. Greer.   (*Amer. J. Pharm.*, 1922, **94**, 80–92.)—Examination of a number of commercial samples of this salt by the titanous chloride and methylene blue method of Knecht and Hibbert (*New Reduction Methods in Volumetric Analysis*) showed a variation in purity ranging from 84·7 to 0·0 per cent.   Those having no reducing power appeared to consist of sodium formaldehyde sulphoxylate, whilst intermediate samples were apparently mixtures of this substance with sodium hydrosulphite, or else deteriorated samples of the latter.   The presence of sodium formaldehyde sulphoxylate was indicated by the increased reduction of methylene blue on raising the temperature.   Various methods were tried for the purification of commercial samples, but with little success, and the authors therefore applied the following laboratory method to the preparation of the salt: Four hundred and twenty c.c. of solution, containing 208 grms. of sodium bisulphite, were heated to 60° C., 140 grms. of sodium chloride added, and the temperature raised to 65° C.   To the mixture 230 c.c. of a solution containing 118 grms. of sodium formaldehyde sulphoxylate, also at 65° C., were rapidly added, and the precipitate of anhydrous sodium hydrosulphite was filtered off in an atmosphere of carbon dioxide, washed with alcohol and ether, and dried in carbon dioxide under a pressure of 15–20 mm. of mercury.   The amount of the product thus obtained ranges from 55 to 60 per cent. of the theoretical quantity, and has a purity of 80–85 per cent.   It is permanent if kept in tightly closed bottles, requires no purification before use, and is free from zinc, but is somewhat more expensive to prepare than by the action of zinc upon sodium bisulphite solution.   Experiments are described showing the toxicity of sodium hydrosulphite and its decomposition products when injected intravenously into rats.   T. J. W.

Preparation of Sodium Hydroxide Solution free from Carbon Dioxide. J. Cornog.   (*J. Amer. Chem. Soc.*, 1921, **43**, 2572-2573.)—Water is boiled in a conical flask, cooled, and ether is added so as to form a layer about 4 cm. in depth. Small pieces of sodium are then dropped into the flask; these pieces fall through the ether, but do not pass into the water.   The water contained in the ether layer causes the slow formation of sodium hydroxide which passes into the lower layer of water.   The ether prevents the results usually observed when sodium is brought into contact with water, and there is no risk of fire or explosion as long as the depth

of ether is sufficient to prevent the sodium from coming into simultaneous contact with air and water. It may be necessary to add more ether to replace that evaporated when the amount of sodium to be dissolved is large. When the desired quantity of sodium has been dissolved, the ethereal layer is removed by means of a pipette, and the last traces by boiling the solution. Sodium hydroxide prepared in this way does not yield a precipitate when treated with barium hydroxide solution. W. P. S.

Estimation of Oxides of Nitrogen. V. C. Allison, W. L. Parker and G. W. Jones. (*U.S. Bureau of Mines Techn. Paper*, **249**, 1–13.)—The oxides of nitrogen in mine air are oxidised to nitrogen peroxide by means of hydrogen peroxide in the presence of sodium hydroxide, and then estimated by a modified phenol-sulphonic acid method. The accuracy is about 5 parts per million. Solutions required are:—*Phenol-disulphonic acid*: Twenty-five grms. of phenol are dissolved in 150 c.c. of sulphuric acid, 75 c.c. of fuming sulphuric acid are added, and the mixture heated for two hours at 100° C. *Nitrate solution*: Potassium nitrate (0·72 grm.) is dissolved in a litre of water, 10 c.c. are evaporated to dryness, the residue moistened with 2 c.c. of the phenol-sulphonic acid, and the solution made up to one litre (1 c.c.=0·001 mgrm. N). *Ammonia solution*: Equal volumes of ammonia solution (0·880) and water. After the ordinary estimations on the air sample in the Haldane apparatus, the level of the mercury in the bottle and in the trough is equalised, and the volume marked at this point; air is allowed to enter and the bottle removed. Five c.c. of 10 per cent. sodium hydroxide solution and 5 c.c. of hydrogen peroxide are added, and the bottle closed with a rubber stopper, rotated, and set aside for 30 minutes. The contents are then washed out, filtered, and evaporated to dryness, and the residue moistened with 2 c.c. of a mixture of equal volumes of phenol-disulphonic acid and sulphuric acid. Ten c.c. of water are added, then 15 c.c. of the ammonia solution, and the mixture diluted to 100 c.c. and matched against an amount of standard nitrate solution, diluted to 100 c.c., to which 5 c.c. of the ammonia solution have been added. The volume of air taken is measured, and the results calculated in parts of NO_2 per million. When 250 c.c. of air are taken 1 c.c. of the standard nitrate solution =7 parts of NO_2 per million. H. E. C.

Separation of Germanium and Arsenic. J. H. Müller. (*J. Amer. Chem. Soc.*, 1921, **43**, 2549–2552.)—Arsenic and germanium may be separated by the action of hydrogen sulphide on a solution of their oxides in the presence of a large excess of hydrofluoric acid, the separation depending on the fact that hydrogen sulphide does not precipitate germanium sulphide from a solution of fluogermanic acid. The solution containing the arsenic and germanium is treated in a platinum basin with an excess of pure hydrofluoric acid, and is then saturated with hydrogen sulphide; the precipitated arsenic sulphide is collected on a filter paper in a platinum funnel, washed first with hydrofluoric acid saturated with hydrogen sulphide, and then with water. The sulphide is dissolved in dilute ammonia solution, the solution evaporated in a silica basin, the residue oxidised with nitric acid, and

the arsenic then estimated as magnesium pyroarsenate. The acid filtrates containing the germanium are evaporated with sulphuric acid in a platinum basin, then diluted with water, rendered ammoniacal and neutralised with hydrochloric acid. Concentrated hydrochloric acid is added in quantity sufficient to make the concentration of the acid about 15 per cent., and the solution is treated with hydrogen sulphide; the germanium sulphide is collected, washed with water saturated with hydrogen sulphide, ignited, oxidised with nitric acid, again ignited and weighed as germanium dioxide. The method is suitable for the estimation of as little as 0·01 per cent. of arsenic in germanium compounds.　　　W. P. S.

Identification of Steels by Means of the Contact E.M.F. Galibourg. (*Comptes rend.*, 1922, **174**, 547–550.)—Application of the Brinell hardness test to the reheated metal permits of the approximate identification of different classes of ordinary steels, but not of special steels. With the latter, further information is furnished by determination of the contact electromotive force. In a bath of mercury heated at 120° C., by means of a nichrome resistance, is immersed an electrolytic iron wire which is connected with one terminal of a millivoltmeter. The other terminal of the latter is connected with a metallic clamp, which is cooled by circulating water and holds the test piece; the end of this piece also dips into the mercury. After four or five seconds, when the needle of the millivoltmeter becomes still, the reading is taken. The values of the contact e.m.f. at various temperatures ranging from 20° C. to 320° C. have been measured in this way. Tempering affects the course of the temperature-e.m.f. curve but slightly.

　　　　　　T. H. P.

Estimation of Aluminium, II. L. Losana. (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 3–4.)—In this method the hydrogen evolved when aluminium is heated with an alkali hydroxide solution (*cf.* ANALYST, 1921, **46**, 383) undergoes combustion in presence of palladium asbestos, and the water thus formed is absorbed and weighed. The reaction flask is fitted with a three-holed rubber stopper carrying a glass tube and a tapped funnel, both reaching nearly to the bottom of the flask, and a reflux condenser. The latter is joined successively to a ∪-tube charged with pumice moistened with sulphuric acid; a ∪-tube containing, in one limb, first dry granulated calcium chloride and then phosphoric anhydride, and in the other a number of fine gauze discs to prevent back-firing; a horizontal glass tube about 15 cm. long, charged with palladinised asbestos and drawn out fine at its further extremity, and surrounded by a spiral of nichrome or other resistance wire, by means of which the asbestos is kept at about 200° C.; two ∪-tubes containing calcium chloride and phosphoric anhydride respectively.

　　From 0·5 to 1 grm. of the aluminium alloy turnings is placed in the reaction flask with a little water, a slow current of air passed through the apparatus, and the asbestos tube then heated. Potassium hydroxide solution is introduced slowly into the flask through the funnel, so that the evolution of hydrogen is gentle and regular. When the reaction is complete the contents of the flask are boiled for a time, and the current of air maintained for 15 minutes. Multiplication

by 1·0036 of the weight of water obtained gives the weight of aluminium in the sample. The method gives results in good agreement with those obtained by estimating the aluminium by difference. T. H. P.

Co-precipitation of Vanadic Acid with Ammonium Phosphomolybdate. **J. R. Cain and J. C. Hostetter.** (*J. Amer. Chem. Soc.*, 1921, **43**, 2552–2562.)— A method described previously (ANALYST, 1912, **37**, 284) for the estimation of vanadium depends on the precipitation of vanadic acid together with ammonium phosphomolybdate. Investigation of the mechanism of this reaction shows that the co-precipitation of the vanadic acid results from a partition of the latter in some undissociated form between the solution and the solid phase. The maximum absorption by the solid phase occurs at 40° to 50° C. and in a 2 *N* nitric acid solution. Dilution decreases the absorption, but this effect is minimised by the presence of ammonium nitrate. W. P. S.

Estimation of Hydrosulphurous and Sulphoxylic Acids. F. De Bacho. (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 501–502.)—This method is based on the fact that hydrosulphite forms with excess of formaldehyde a solution highly resistant to oxidation by atmospheric oxygen, whereas pure sodium hydrosulphite solution undergoes rapid change, owing partly to oxidation and partly to intramolecular conversion into sodium metabisulphite and thiosulphate. In presence of excess of formaldehyde, sodium hydrogen sulphite and sodium metabisulphite act neither on iodine nor on sodium hydroxide in dilute solution, and sodium sulphite, transformed into sodium hydrogen sulphite by means of sulphuric acid, exerts no influence on these solutions. The action of sodium thiosulphate on the reaction cannot be avoided, but the amount of this salt present may be determined exactly. Decinormal iodine and sodium (or barium) hydroxide solutions are used, and the reactions taking place are:

(1) $Na_2S_2O_4 + 3H_2O + 4I \longrightarrow NaHSO_4 + 4HI + NaHSO_3;$
(2) $NaHSO_2 + 4I + 2H_2O \longrightarrow NaHSO_4 + 4HI;$
(3) $NaHSO_4 + 4HI + 5NaOH \longrightarrow Na_2SO_4 + 4NaI + 5H_2O;$
(4) $2Na_2S_2O_3 + 2I \longrightarrow Na_2S_4O_6 + 2NaI.$

About 1 grm. of sodium hydrosulphite, or 1 to 2 grms. of sodium formaldehyde sulphoxylate, is dissolved in a weighing bottle in 10 c.c. of pure 40 per cent. formaldehyde solution and, if necessary, 5 c.c. of water, the bottle being then left closed for about 20 minutes. The solution is next transferred quantitatively to a 500 c.c. measuring flask, together with 150 to 200 c.c. of water, two drops of 0·1 per cent. methyl orange solution and sufficient *N*-sulphuric acid to render the reaction distinctly acid; any marked excess of acid must be avoided. To 50 c.c. of the solution are added two drops of phenolphthalein solution, 0·1 *N*-sodium hydroxide solution free from carbon dioxide or 0·1 *N*-barium hydroxide solution being then run in until the colour changes to pink; the liquid is then titrated with 0·1 *N*-iodine solution in presence of starch paste. In absence of thiosulphate or with sulphoxylates of low grade, satisfactory results are obtained. If such is not

the case, the solution is decolorised with a drop of thiosulphate solution and then titrated with carbon dioxide-free 0·1 N-sodium or barium hydroxide solution; for the second titration the water used must be free from carbon dioxide and the iodine solution must contain no free acid. The acidity formed during the titration with iodine solution is the basis for the calculation of the content of $Na_2S_2O_4$ or $NaHSO_2$, one-tenth of an equivalent of NaOH corresponding with one-fiftieth of an equivalent of $Na_2S_2O_4$ or $NaHSO_2$. The content of sodium thiosulphate is calculated by subtracting four-fifths of the number of c.c. of sodium hydroxide used from the number of c.c. of iodine solution employed. This method yields highly concordant results. T. H. P.

Argentometric Titration of Phosphoric Acid. I. M. Kolthoff. (*Pharm. Weekblad*, 1922, **59**, 205–215.)—In estimating phosphoric acid by titration with silver nitrate the best results are obtained by rendering the liquid neutral to phenol red after adding the excess of silver nitrate. Phenolphthalein is less suitable as an indicator. The free acid formed in the reaction may also be removed by adding about 2 grms. of sodium acetate per 10 c.c. of a 0·1 molar solution of phosphate, and this addition prevents the interference of ammonium, calcium and magnesium salts. In the case of urine the phosphoric acid is first precipitated as ammonium magnesium phosphate, the precipitate dissolved in the smallest possible amount of nitric acid, and the solution neutralised, with dimethyl yellow as indicator. Excess of standard silver nitrate solution is now added, then sodium acetate (2 grms. for 50 c.c. of urine), the mixture filtered, and the excess of silver in the filtrate titrated by Volhard's method.

Apparatus.

Preparation of Flexible Collodion Membranes. J. M. Looney. (*J. Biol. Chem.*, 1922, **50**, 1–4.)—Five grms. of pyroxylin, dried for two days over sulphuric acid, are thoroughly moistened with 25 c.c. of absolute alcohol and completely dissolved by the addition of 75 c.c. of ether distilled from sodium. To the solution 15 c.c. of ethyl acetate are added, the liquids well shaken together, and the solution allowed to stand overnight, after which the clear supernatant liquid is decanted for use. The solution is poured into smooth, clean and dry test tubes or flasks, and the excess poured out, the vessel being inverted until the collodion membrane is quite dry, this stage being accelerated, if necessary, by passing a current of air through the vessel. The dry membrane is loosened from the neck, and a gentle stream of water is passed between it and the wall of the vessel, when the membrane may be removed. These membranes may be rolled up into small balls without damage and retain their permeability after drying for two weeks at room temperature. T. J. W.

Reviews.

ANALYTICAL CHEMISTRY. Vol. I.: Qualitative. By F. P. TREADWELL, Ph.D.
Translated and Revised by W. T. HALL. Fifth English Edition. Pp. 573.
New York: John Wiley & Sons; London: Chapman & Hall. 1921. Price
23s. net.

Unless a student of chemistry has a good working knowledge of the physico-
chemical principles underlying reactions, there is every likelihood that to him
qualitative analysis will be more or less an unintelligent application of the analytical
processes given in text-books. Such a training, besides being of doubtful value
from an educational point of view, is scarcely conducive to the making of a good
analyst; it being vital that he should understand as much as possible each process
he employs to enable him to carry it out most efficiently. Attaching due im-
portance to the value in qualitative analysis of these physico-chemical conceptions,
Professor Hall departed somewhat from the text of Treadwell in preparing the
previous edition, and, in addition to incorporating an account of these theories,
rendered the work more comprehensive by revising the whole text in accordance
with them. In the preface of the present edition he states that the annual sales
of the book in its revised form have been more than doubled—a point which
speaks for itself.

The scope of the volume is essentially the same as that of the former edition.
The work has, however, been brought up-to-date, apparently by comparison with
the latest edition of Fresenius' Qualitative Analysis, and, moreover, several useful
alternative separation tables have been added. These tables have been taken
from the 1919 edition of Noyes' Qualitative Chemical Analysis, and have been
carefully investigated by A. A. Noyes and his collaborators. The student thus
finds himself confronted with the choice of several methods, but with very little
information relating to their peculiar merits. It is stated, on page 199, that "one
scheme is best under certain conditions, and another scheme under different
conditions." This statement is substantiated by reference to such phenomena
as the carrying down of zinc and magnesium by chromium when precipitated as
hydroxide by the addition of excess of ammonium hydroxide in presence of am-
monium chloride. To a large extent, the success of an analyst depends upon how
far he overcomes difficulties of this nature, yet the instance quoted is the only
attention paid to this important problem of occlusion by gelatinous precipitates;
no reference having been made to it in Part I. on "General Principles." Reference
could well have been made to the recent investigation by Yasui (Mem. Coll. Sci.,
Kyoto, 1919, 4 (2), 65–67) on the attempted separation of the hydroxide of zinc
from that of chromium, in which he found that very considerable amounts of zinc
were retained, even after three treatments of the precipitate of chromium hydroxide.

It seems more desirable that one scheme of analysis, with full details of its
defects, should be given, and this the student should be advised thoroughly to
comprehend and to adopt, after having made himself conversant with the tests

for the ions. Then he will be in a position to appreciate other schemes, or even to devise suitable methods to eliminate difficulties, which may arise. Subsidiary schemes, therefore, should be accompanied with notes on their particular uses. Apart from these remarks, the various procedures given are exceptionally well described.

A few minor faults appear in the arrangement of the work. Surely the place for the very fine description of Spectroscopic Analysis, which is given under the reactions for barium, is in the section on "General Principles." Again, the reactions of hydrogen peroxide are given under "Sodium." Should they not be inserted in the part on "Anions," viz. Part III.?

Although the work has been largely modernised, a few instances appear in which the translator, or rather the reviser, has too rigidly adhered to the original text, and has consequently described processes which now seem quaint. In Part I., on "General Principles," we are told at great length how to carry out reductions on charcoal sticks obtained from splinters having good, straight fibres such as old-fashioned brimstone matches. Incidentally, these reactions are described as "exceedingly beautiful reactions and are among the most sensitive . . . and should be faithfully practised by every beginner." Borax beads are rendered sticky "by moistening with the tongue," in order that the substance to be tested may adhere.

The work is remarkably free from errors. The following point, however, should be mentioned. Equations illustrating reactions in which basic salts are precipitated give definite formulae for the basic salts as if they were well-defined compounds. As examples, the following may be quoted:—$Co(OH)Cl$, $Zn_2(OH)_2CO_3$, $Ni_2SO_4(OH)_2$, $Cu_2(OH)_2SO_4$, $Al(OH)_2C_2H_2O_2$, $Fe(OH)_2C_2H_3O_2$, and $Mg_4(CO_3)_3(OH)_2$. In one case only, viz. the last, is it pointed out that the "composition of the precipitated salt varies with temperature and concentration," but, in spite of all this, the "salt" represented is "often obtained." Judging from the number of times the word "molal" is found, it appears to have taken the place of the generally accepted term "molar," although the latter word is sometimes found in the text. The unnecessary adoption of such new terms is not desirable.

On the whole, the work has been compiled on modern lines, and will continue to rank as a standard work on the subject of Qualitative Analysis.

HUBERT T. S. BRITTON.

ORGANIC SYNTHESES. Vol. I. ROGER ADAMS, Editor in Chief. New York: John Wiley & Sons; London: Chapman & Hall. 1921. Price 8s. 6d. net.

Ever since 1914 the supply of organic chemicals for research and other purposes has been a matter of great difficulty. Even when supplies were available the cost was in many cases prohibitive, so that the chemist was compelled to prepare his own reagents: his troubles did not end even here, for he was faced with the further difficulty of the incompleteness or even total absence of instructions for their preparation. It is to overcome these difficulties that this book is written. The intention of the authors, or rather editors, is, that it should be the first of a

series of volumes appearing annually, and each containing instructions for the preparation of about twenty compounds in quantities up to about five pounds. A number of chemists have taken part in the work: each preparation has been thoroughly worked out by two of them and their results checked by two others.

All concerned in the compilation of this volume may be congratulated. The instructions are clearly given, and useful notes are added on points of importance; there are abundant references to original papers; where necessary, simple diagrams are given of a suitable form of apparatus; the printing and general style leave nothing to be desired. One of the most noticeable features is the very satisfactory yields stated to be obtained—in nearly every case over 90 per cent. of theory. This suggests that it is only the absence of exact knowledge on points of detail that causes the poor yields in such a large number of organic preparations, and raises the hope that a time will come when a yield of less than 90 per cent. will be the exception rather than the rule.

As a book of instruction for students, this volume is not likely to be of much value, as it deals mainly with compounds not usually prepared by students. The small amount of ground covered naturally limits its usefulness also to the manufacturer and research chemist; but, as years pass and succeeding volumes are added to the first, the series will be of the very greatest utility, and should find a place in every organic laboratory.

The editors welcome the assistance of any chemist who can contribute details of improved methods or make any suggestions that will add to the value of the series. A. F. KITCHING.

AN INTRODUCTION TO THE PHYSICS AND CHEMISTRY OF COLLOIDS. By EMIL HATSCHEK. Fourth Edition (entirely re-written and enlarged). Pp. xiii +172. London: J. & A. Churchill. 1922. Price 7s. 6d. net.

The first edition of this book appeared in 1913, and at once gained approval and popularity, which has increased with each succeeding edition. The present volume has been entirely re-written and enlarged, and is the best introduction the student could have to the fascinating field of colloids. The book is very readable, accurate and up to date, and surveys in excellent fashion the present position of the more salient points in colloid physics and chemistry. Especially good are the sections dealing with viscosity, gels, adsorption and emulsions. The latter subject is only now finding its way even into the larger text-books, and Mr. Hatschek's summary is thus all the more valuable to the beginner.

The text discusses many standing difficulties in colloid theory, and points out several interesting lines for further research. The reviewer, however, was surprised to find no mention at all of Loeb's work on the influence of hydrogen-ion concentration in protein studies (especially with gelatin), although the so-called Hofmeister and Pauli series receivè due attention, and the obvious difficulties involved are evidenced.

The binding, printing and illustrations are very good indeed, and it has been a distinct pleasure to read the book. WILLIAM CLAYTON.

POISONS: THEIR EFFECTS AND DETECTION. By ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., and MEREDITH WYNTER BLYTH, B.A., B.Sc., F.I.C. Fifth Edition. London: Charles Griffin & Co. 1920. Price 36s.

This edition of "Poisons" retains the general design of previous editions, but, as stated by the authors in their preface, some work has been omitted and replaced by more modern methods.

The short, but interesting Part I., deals with the old poison lore, and gives a brief account of the growth of modern methods of toxicological analysis. The appendix of the earlier editions (dealing with antidotes) has been omitted in the present volume.

The present edition of this book contains a large number of references, as in the case of the previous edition, but, although certain modern references are given, very many are far from recent; it is somewhat mis-leading to refer to a method of 1893 as a new method (as is done on page 551, dealing with oxalic acid). Several instances of this character detract, to some extent, from the value of the work.

Considerable stress is laid by the authors on micro-chemical methods for the detection of poisons; this addition to the present work, and will be very welcome to many who may be confronted with the detection of minute quantities of poisons (especially organic) in viscera.

The various poisons are dealt with at fair length in most cases, and some very fully. The reader, however, misses with regret one or two, the inclusion of which would have enhanced the value of the book. Some reference to hydro-quinone and the other di-phenols would have been welcome; but no mention, apparently (excepting very indirectly) of these three di-phenols is made, not-withstanding their toxic properties, and the frequent use of at least one of them (hydroquinone).

It is to be regretted that some errors present in previous editions still remain in the revised volume. For instance, in the description of the iodic acid test for morphine, it is stated that "if morphine be present, the carbon disulphide *floats to the top* distinctly coloured pink." It is rightly pointed out in the present edition that "other substances, however, also set free iodine from iodic acid"; but in mentioning the further test, namely, the after-addition of ammonia, it would have been of interest if the reference had been given respecting the authority for the somewhat curious statement that "*the pink colour of the carbon disulphide is deepened* if morphine was present; on the contrary, if morphine was not present, it is either discharged or lessened."

The authors in the present edition again refer in several cases to another of their publications ("Foods") for a description of the method of analysis to be employed. It is perhaps unfortunate that they could not see their way to describe the methods in the present volume of *Poisons*.

The book will be found a valuable one for reference, notwithstanding the

above blemishes; many methods of analysis are described, and, although frequently no guide is given as to the most reliable, this may not be disadvantageous, since it tends to cause the reader to carry out the various methods, and thus find the method which gives the most reliable results.

JOHN WEBSTER.

PETROLEUM. By SIR BOVERTON REDWOOD, Bart., D.Sc., F.R.S.E., F.I.C., &c. Fourth Edition. Three volumes. Pp. 1353 (with plates and maps). London: Chas. Griffin & Co. 1921. Price £5 5s. net.

So far as it is possible to embody in a single treatise existing knowledge in a technical subject, Sir Boverton Redwood's treatise on "Petroleum" is one of the most complete. In the mass of detailed information which it contains on all branches of the subject, it reminds one of the classical volumes on metallurgy written by the late Dr. Percy, and is itself a classic on the subject of which it treats.

The present edition is noteworthy in many ways. Not only has it been very thoroughly revised and largely re-written, with the help of a number of friends and colleagues of the author, whose names are a sufficient guarantee of their competence, but this laborious work was carried nearly to completion during the war, and the author was engaged in finishing it up to within a few days of his death, which occurred quite suddenly in June, 1919.

The general plan of the book remains the same as in former editions. The first two sections deal with the History and Distribution of Petroleum, and, in view of the rapid development of this industry in recent years, it is not surprising that these chapters have more than doubled in size since the first edition was published in 1896. The first petroleum well was drilled in 1859, and the entire modern petroleum industry has arisen during the lifetime of the older members of the present generation.

Sections 3 and 4, on the Physical and Chemical Properties and Origin of Petroleum, have been largely re-written by Prof. Brame and Dr. Dunstan, and their work has been as thoroughly done as one would expect. All the most important work, up to the date of the revision, will be found, either in the text or in the numerous references to original papers.

Sections 5 and 6, describing the methods adopted in different countries in the production and refining of the crude oil, have also undergone considerable expansion. There is a little overlapping on pages 517–18 and 525–6, the refining processes of Edeleau, Macalpine and Adiyasievitch being described twice over.

Section 7, on the Shale Oil and Allied Industries, has been completely revised and largely re-written.

Section 8 is devoted to the Transport, Storage and Distribution of Petroleum. In the United States, nearly 45,000 miles of pipe line are now in use, the total daily capacity of which is two million barrels. Some of the pages of this section

most useful to the analyst are pp. 696–713 on fire and explosion risks connected with petroleum vapour and mixtures of the vapour with air.

Section 9, on Testing Methods, to which the analyst will most frequently refer, contains a description of the principal tests applied in the examination of crude oils, fuel oils, lubricating and illuminating oils, residuum, paraffin and asphalt. Reference is made on page 831 to the advantage which attaches to the expression of viscosity values in absolute measure. A panel appointed by the British Engineering Standards Association is now engaged in the consideration of this subject, and it is to be hoped that the work of this panel may lead to the employment of more uniform methods of measuring viscosity, with easily manipulated apparatus based upon correct scientific principles, and to the expression of results in terms which will be as readily intelligible as those in which other physical properties such as density are expressed. The author's remarks (pp. 842–847) on the viscosity test in relation to friction-testing machines, though written many years ago, are still of interest and importance. In nearly all the machines which he describes, the oil is tested under conditions which measure only the friction due to its viscosity, hence the apparent close relationship between the viscosity and lubricating power to which he refers on page 846. The property of "oiliness," which is now recognised as of very great importance, has no connection with viscosity, and is not measured by these machines as they are generally used.

Section 10, on the Uses of Petroleum and its Products, revised by Prof. Brame, is one of the most interesting and valuable sections of the book. Some useful though brief remarks on Switch and Transformer oils, by Mr. Pollard Digby, will be found on pp. 887–889, and a sub-section on Casing-head Gasoline on pp. 934–939. The manufacture of "lampblack" from natural gas, usually known as "carbon black," is briefly described on pp. 939 and 940. There is a good sub-section on Petroleum as Fuel on pp. 940–965; and one on Petroleum Engines, by Mr. Worby-Beaumont, on pp. 965–978.

In the last section and appendices will be found the various regulations, British and foreign, relating to the testing, storage, &c., of petroleum and its products, Thames Conservancy Bye-Laws, Statistics of Production, and the Import Duties levied in different countries. A valuable Bibliography by Mr. W. H. Dalton, which occupies 163 pages, and includes 8804 references, and a good index, complete the work. In a Foreword to the first volume, Sir Fredk. Black has contributed a brief biographical notice of the author, which will be read with interest and appreciation by all who knew him. Much credit is due to the publishers for their enterprise in publishing this costly work, providing new maps, &c., and to all those who have been responsible for the correction of proofs, which appears to have been exceedingly well done.   L. ARCHBUTT.

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Publications Received.

COLLOID CHEMISTRY OF PROTEINS. By Prof. W. PAULI. Translated by P. C. L. THORNE, M.A., A.I.C. Part I. Pp. xi+140. London: J. & A. Churchill. 1922. Price 8s. 6d. net.

A COURSE OF PRACTICAL ORGANIC CHEMISTRY. By T. SLATER PRICE, O.B.E., D.Sc., F.I.C., and W. F. TWISS, D.Sc., F.I.C. Pp. xiii+239. London: Longmans, Green & Co. 1922. Price

DER GEBRAUCH VON FARBENINDICATOREN. By I. M. KOLTHOFF. Pp. 144. Berlin: J. Springer. 1921. Price 47M.

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. By J. W. MELLOR, D.Sc. Vol I., pp. 1065; Vol. II., pp. 894. London: Longmans, Green & Co. 1922. Price £3 3s. each Vol.

Vol. I. deals with general inorganic and theoretical chemistry, and with hydrogen and oxygen and their compounds.
Vol. II. deals with the halogen elements and the alkali metals.

APPROVED TECHNIQUE OF THE RIDEAL-WALKER TEST. By S. RIDEAL, D.Sc., and Capt. J. T. A. WALKER, R.A.M.C. Pp. 12. London: H. K. Lewis & Co. Price 1s. net.

Contains a bibliography of publications relating to the test.