DECEMBER, 1917. Vol. XLII., No. 501.

THE ANALYST.

OBITUARY.

CORPORAL JOSEPH ARTHUR BROWN.

J. A. BROWN was killed in action on April 20, in his thirty-seventh year. Trained at University College, Nottingham, he was articled in 1897 to Mr. John White, Public Analyst for Derbyshire, and in 1902 was appointed chief assistant to Mr. R. A. Cripps, Public Analyst for Bournemouth. In 1910 he became chief assistant to Mr. C. C. Duncan, Public Analyst for the County of Worcester, relinquishing this post in 1914 in order to become assistant to Mr. J. F. Liverseege, City Analyst for Birmingham. He communicated several papers to the Journal of the Society of Public Analysts and to the *Chemical News*. He was elected a Fellow of the Institute of Chemistry in 1904. At the outbreak of war he enlisted in the 1st Birmingham Battalion (*Proc. Inst. Chem.*, 1917, part iii., p. 15).

GEORGE HOLLOWAY.

A good man has gone from us, and the writer's grief is as great as that of many others of his friends, and they are many indeed.

Holloway was born in 1863 and died on October 24 of this year, happily only after accomplishing the greatest work of his life. His life's work may be summarised thus:

After an admirable academical career under such distinguished teachers as the late Sir Edward Frankland and Sir Edward Thorpe, he applied himself to consulting and metallurgical practice, and diligently occupied himself with the interests of his profession.

Handicapped as he was by physical disablement, he never lost heart, and was of unfailing cheerfulness and sympathy towards others who had even less ground for complaint.

At one time he had some thought of accepting a Chair in his own subject, but his mind was not of the academic class—it was too broad.

As an illustration of his breadth of view, the scope of his papers, ranging from the chemistry of petroleum to that of the most recondite minerals, could be cited.

Many of those who read this tribute have had occasion to consult him on difficult metallurgical questions. His invariable courtesy in affording aid, and his readiness to help in obtaining samples of ores and like materials not of the ordinary class and difficult to get at short notice, showed just that spirit of mutual help which should inform and animate a liberal profession.

In 1915 Holloway was sent to Canada as Chairman of a Commission appointed to decide whether nickel could not preferably be refined in the country of its origin. After many months' work the labours of the Commission were embodied in a large volume as different from the ordinary Governmental Report as can well be imagined. It is a live statement, clear and to the point. It is also *très documentée,* and reference to any part of a most intricate and important subject is simple. In fact it is a classic.

Finis coronat opus, or, better, *Opus coronat finem.*

BERTRAM BLOUNT.

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

AN ordinary meeting of the Society was held on Wednesday evening, November 7, in the Chemical Society's Rooms, Burlington House. In the absence of the President the chair was occupied successively by Mr. A. Chaston Chapman, F.I.C., and Dr. Bernard Dyer, F.I.C., Past-Presidents.

The minutes of the previous ordinary meeting were read and confirmed.

Certificates of proposal for election to membership in favour of Messrs. Kendall Colin Browning, M.A. (Cantab.), 11, Barton Terrace, Dawlish, Government Analyst, Ceylon; Henry Edward Cox, B.Sc. (Lond.), A.I.C., 8, Risca Road, Newport, Mon., Deputy Agricultural Analyst for the County of Monmouth, chief assistant to Mr. G. R. Thompson, F.I.C.; Frederick William Edwards, 283, Friern Road, Dulwich, assistant to Mr. P. A. Ellis Richards, F.I.C.; John Monteath Guthrie, 199, Ferry Road, Leith, chief chemist to Messrs. Wm. McEwan and Company, Ltd., Fountain Brewery, Edinburgh; Frederick Thomas Munton, A.R.S.M., Rosslyn, Winsford, Cheshire, chief chemist to the Salt Union, Ltd.; Leonard Owen Newton, 29, St. Mildred's Road, Lee, S.E., chief chemist to Messrs. Sofnal, Ltd., Westcombe Hill, Greenwich, S.E.; and Ernest Walter Wright, 179, Edgware Road, W., analytical chemist, were read for the first time.

Messrs. C. V. Bacon and K. H. Vakil, B.A., B.Sc. (Tech.), were elected members of the Society.

The following papers were read: "Note on Jets for Burettes," by J. H. Coste, F.I.C.; "Analytical Examination of Acorns and Chestnuts," by Julian L. Baker, F.I.C., and H. F. E. Hulton, F.I.C.; and "The Reductase Test for Milk," by Paul S. Arup, B.Sc., A.I.C.

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ANALYTICAL EXAMINATION OF ACORNS AND HORSE CHESTNUTS.

(*Continued from p.* 355.)

By JULIAN L. BAKER, F.I.C., AND H. F. E. HULTON, F.I.C.

(*Read at the Meeting, November* 7, 1917.)

Discussion.

The Chairman (Mr. A. Chaston Chapman), in inviting discussion, remarked on the high proportion of matter soluble in cold water in the sample of chestnuts No. 2. After allowing for reducing sugars and other known substances that would be soluble in water there would still be a large amount left unaccounted for, regarding which any available further information would be very acceptable. The direction of attention to the fact that the Lintner method for the estimation of starch was one to be adopted with very great caution was an important point in the paper. The method was a very convenient one, and was widely used; and for materials of fairly well-known composition, it possessed obvious advantages in regard to simplicity and speed; but with substances of more or less unknown composition, it might clearly be liable to serious error. This had been pointed out previously, but in these analyses of chestnuts and acorns the discrepancies were particularly striking. Although the authors had been unable to detect any starch-splitting enzyme in the acorn, it would be very strange if there were not some provision for converting the acorn starch into something soluble and assimilable. He hoped, therefore, that the authors might be able to continue their researches, and see whether there was not an enzyme capable of acting on the acorn starch, even though it might have no action on potato starch.

Colonel Vernon said that these analyses were particularly interesting from the point of view of the food value of these two products, the collection of which was being urged by the Government. The results of No. 2 of the horse chestnut analyses seemed to suggest in that case some germination had taken place, the reducing matter having increased and the starch diminished. As to the occurrence of an enzyme in the acorn, he thought that there must be something which would produce more feeding material for the young plant than was at present apparent. The acorn, however, was somewhat peculiar in its mode of growth. It grew from the surface of the soil, sending its roots down; if it got below the surface it would not germinate.

Mr. A. E. Parkes asked whether the authors had examined the acorns for tannic acid. He had recently made some partial analyses of chestnuts and acorns, with results differing slightly in some respects from those of the authors, and in the case of the acorns a considerable quantity of tannic acid had been found.

Mr. G. N. Huntly asked whether the authors could give any approximate idea of the amount of saponin that was present in horse chestnuts. It was known that its presence rendered the nuts unfit for food.

Mr. Hulton said that if acorns were germinated in water it would be noticed

that there was very little visible depletion of the cotyledons, even up to the time at which the plant was able to grow independently, so that it would appear as if only a very small proportion of the original starch disappeared by the time that the leaves had reached the chlorophyll-bearing stage. They proposed to try the action of acorn diastase upon soluble starch prepared from acorn starch.

Mr. C. H. CRIBB asked whether there was any special difficulty in preparing starch from chestnuts or acorns; otherwise it seemed strange that such a source of starch—say, for laundry purposes—had been so long neglected.

Captain C. G. MOOR remarked that the use of acorns was being recommended for feeding poultry, and possibly, if alcohol were manufactured from them, the residue might be used for feeding purposes.

Mr. JOHN HUGHES said that he had found that roasting improved acorns a great deal for feeding purposes, the resulting powder having a sweet and biscuit-like taste instead of the acrid, disagreeable taste of the original acorns. It used to be imagined that acorns were only useful for pigs, and were liable to injure cattle, but if dried and ground as suggested they would form a valuable cattle food, and would certainly be useful for poultry.

Dr. J. A. VOELCKER remarked that the liability of cattle to suffer from acorn-poisoning was well known, though there was some mystery as to the exact cause. The main factor, however, seemed to be the quantity of acorns eaten relatively to that of the other food. In a season in which acorns were plentiful and grass was scarce the cattle might suffer, while under the opposite conditions the quantity of acorns eaten might not be sufficient to cause any trouble.

Mr. BAKER said that in France considerable attention had been devoted to the isolation of starch from chestnuts, though without much commercial success, mainly, he thought, for the reason that, while the crops ordinarily used for starch manufacture were collected in bulk at one spot, the utilisation of products which had to be collected in small quantities over large areas was commercially possible only in times like the present. In ordinary times it was unlikely that chestnuts or acorns would ever pay their way as sources of starch, having regard to all the other sources that were available. The large amount of unaccounted-for material in the cold water extract, particularly in the chestnut No. 2, was not confined to chestnuts or acorns. In cocoa, for instance, the matter soluble in water could not be fully accounted for by the determined constituents, and the same was true of malt extract. In chestnuts and acorns there would be some tannin, but not very much, and glucosides would also be present. Some observers gave the proportion of tannin in horse chestnuts at 10 per cent., but he should think that 2 or 3 per cent. would be more probable. He and Mr. Hulton hoped to do some more work on the subject of the enzymes of acorns. They had thought that some information might be obtained by allowing the whole material instead of its aqueous extract to act on starch, but the results were negative. Acorns allowed to germinate under favourable conditions for two or three weeks made great growth, but showed not the remotest trace of enzyme, either in the soluble or insoluble condition. He did not feel very hopeful about clearing the matter up, because if an isolated enzyme would not act

upon potato starch he should hardly expect it to act with any vigour on any other starch. Acorns had been largely used on the Continent for making a spurious kind of coffee. When roasted they developed quite an agreeable flavour, and it was possible that under some conditions they might form a valuble source of food.

NOTE ON JETS FOR BURETTES.

By J. H. COSTE, F.I.C.

(*Read at the Meeting, November* 7, 1917.)

Few textbooks on volumetric analysis devote much attention to the apparatus required, although the worker in this branch of analysis is absolutely dependent upon his appliances. Sutton and Treadwell and Hall are honourable exceptions to this neglect, but neither work deals with the question of jets for burettes and graduated pipettes. The latter authors do indeed say (ed. 1911, p. 527) "it is advisable . . . to have the tip so narrow that it will take eighty seconds for 50 c.c. to run out."

The average 50 c.c. burette has a jet which will deliver drops of about 0·05 c.c.* This allows $\frac{1}{1000}$ of the capacity to be added at a time, and if 50 c.c. or thereabouts are needed for the titration, the delicacy of delivery is probably sufficient. In the case of smaller burettes, which it is often desirable to use, or when only relatively small volumes are delivered from the 50 c.c. burette, a much greater sensitiveness is to be desired. This is not difficult to attain if care is taken in drawing out a jet. To be satisfactory for delicate work with small quantities, a jet must deliver a sufficiently rapid stream, and, when the rate of flow is checked, allow the solution to fall in a succession of small drops. The drop should be as small as the limit of accuracy of the burette.

The usual form of jet is made of thick-walled glass—probably with a view to strength—say, about 3 mm. external and 1 mm. internal diameter. Tap burettes are frequently provided with an inconvenient and undesigned air trap under the barrel of the tap. Drawing out the jet in the flame does very little good, as its principal effect is to reduce the rate of delivery. The influence of the jet on the size of the drop is determined by its external cross-section.

I give on p. 386 results obtained with several jets made by myself.

The tubes marked with an asterisk were elliptical to the extent indicated. The drop and time measurements were made with a 10 c.c. burette, the length of the graduations being 295 mm., so that a good reading to $\frac{1}{100}$ c.c. could be made. Measurements were made from zero in each case. The rate of dropping was from 1 to 2 drops a second. The diameters were determined by means of a microscope with eye-piece micrometer.

* Waxing the exterior of the jet of such a burette reduced the size of the drops from 0·046 to 0·037 c.c.

Jet No.	*Diameter of Jet at Tip.*		*Volume of 100 Drops distilled water.*	*Time of Outflow of 10 c.c., Stopcock Fully Open.*
	External.	*Internal.*		
	mm.	mm.	c.c.	Seconds.
1	1·22	·66 – ·58*	2·14	30
2	1·42	·80	2·61	17
3	0·70	·40	1·40	100
4	1·44	·83	2·60	15
5	1·23	·80 – ·72*	2·18	20
6	1·11	·71	2·10	29
7	1·11	·72 – ·64*	2·10	25
8	1·30	·76 – ·66*	2·20	18
9	1·24	·82 – ·72*	2·37	23
10	0·62	·38	1·35	75
11	1·32	·76 – ·68*	2·44	26
12	1·22	·54 – ·82*	2·31	35
13	0·46	·26	1·43	170
14	0·98	·54 – ·46*	1·80	40
15	0·46	·24	1·00	No continuous flow
16	0·70	·46	1·53	49

No. 13 was drawn out and the tip further constricted; the only effect of this was to make the flow intolerably slow. The drop crept well above the extreme tip, and was formed on the thicker part. The others gave from 38 to 74 drops to 1 c.c. at rates of flow ranging from fifteen to seventy-five seconds.

The National Physical Laboratory allow for burettes and graduated pipettes the following errors:

Capacity greater than millilitre	—	2	10	30	50	75	100	200
And up to millilitre	2	10	30	50	75	100	200	300
Tolerance for content and for delivery ± millilitre ..	0·008	0·02	0·03	0·04	0·06	0·08	0·12	0·18

"The tolerances for graduated apparatus apply to the total volume and to all fractions of the volume not less than one-half of the total volume of the apparatus. For volumes less than one-half the total volume, the tolerance is one-half that for the total volume" (Metrology Pamphlet, p. 39).

The delivery of some of these jets—viz., Nos. 1, 2, 4, 5, 6, 7, 8, 9, 11, and 12—would therefore be insufficiently sensitive for the best use of a 50 c.c. (millilitre) N.P.L. burette if less than 25 c.c. were needed for a titration, and all but No. 15 insufficiently sensitive for a 10 c.c. burette when less than 5 c.c. were needed. On the other hand, the delivery of Nos. 2, 4, 5, 8, and 9 is more rapid than is specified for a small burette, the limits ranging from twenty-five seconds for one with a length of graduations not greater than 200 mm. to seventy for one up to 700 mm.

As a practical conclusion one may state that, since the ultimate unit of delivery

from a burette or graduated pipette is the drop, it is desirable, where the sensitiveness of the indicator used in a titration allows the worker to make the fullest use of the accuracy of his apparatus, that the drop should be as small as possible. It may be reduced by the use of a fine thin-walled jet with a fairly long cylindrical capillary to a volume nearly approaching the limit of accuracy of a N.P.L. marked burette. I may call attention to useful papers on drop-measuring devices by R. Donald (*Proc. R. S.*, B. LXXXVI., 198, 1913; *Lancet*, May 24, 1913, p. 1447; *ibid.*, December 4, 1915, p. 1243).

Discussion.

The Chairman (Mr. A. Chaston Chapman), in inviting discussion, remarked that in the National Physical Laboratory specification he had been informed that nothing was laid down as to the rate at which the burette was to be discharged. In ordinary laboratory practice there might, without going to extremes, be a good deal of variation in the rate of discharge. The limits of "tolerance" laid down were practical limits, the observance of which he should consider essential in a satisfactory burette, but they did not seem to meet the whole case, because a burette might deliver its whole contents within a "tolerance" limit of, say, 0·06 c.c. on 50 c.c., and yet might be distinctly inaccurate at some parts of the scale.

Mr. Coste having pointed out that in the National Physical Laboratory specification there was a provision that in the process of calibration the burette should be allowed to drain for a certain time.

Mr. W. T. Burgess remarked that the allowance for draining would probably equalise any difference due to variation in the rate of discharge.

Mr. Chapman agreed, but observed that that would not apply to the question as to whether the bore was truly cylindrical all the way down.

Mr. G. N. Huntly thought that the point would be covered by the time specified for draining, since the reading would be the same whether a given quantity of liquid was run out rapidly and then, for example, thirty seconds allowed for draining, or whether the discharge was spread over the thirty seconds.

Mr. Chapman: But would thirty seconds be sufficient for, say, 50 c.c. .

Mr. Huntly said that with a definite period for draining the results would be consistent, and if the draining period were properly studied it ought to cover the whole point. He did not entirely agree with Mr. Coste as to the advantages of a jet of small cross-section, as the surface tension of the liquid was also one of the factors controlling the size of the drop. He had tried the use of jets of very small diameter, but the smallest capillary tubes he had been able to make satisfactorily were never below 0·02, and more often 0·025 to 0·03. Ordinary burettes were never less than 0·05, and 20 to 25 drops to the c.c. seemed to be about the general average. It was, however, quite possible to take off and wash down a fraction of a drop, and by doing this one could, even though the jet was larger, work to $\frac{1}{100}$ c.c. The degree of accuracy, therefore, need not necessarily be limited by the size of the drop, though he agreed that this was the case if the drop were not split. A jet too finely drawn out was rather trying to work with, and he thought that for

ordinary work 0·05 was quite small enough. 1 in 1,000 probably represented the extreme practicable limit of accuracy on a full burette, and this was only attainable by applying a temperature correction.

Mr. W. T. BURGESS remarked that burettes drawn out so finely as to deliver drops much smaller than the ordinary average of 20 per c.c. had the disadvantage of being very fragile. He had been able, by himself drawing out the points somewhat, to make burettes deliver drops of about the order of $\frac{1}{40}$ c.c., and such burettes worked well. They were, however, very fragile, and probably, if they were ordered from the maker with such fine points, a considerable proportion would be delivered broken.

Mr. COSTE, in reply, said that he agreed with Mr. Huntly, and had stated in the paper that 1 in 1,000 was a reasonable high degree of accuracy, but it was not always that as much as 50 c.c. was used for a single titration, and a degree of accuracy of delivery that was tolerable on 50 c.c. might not be tolerable on a smaller quantity. Although, as Mr. Huntly had said, a portion of a drop could be taken off, he did not think that was as satisfactory in titration as making the final addition drop by drop. If Mr. Huntly had not succeeded in drawing out the smallest jets, it was, perhaps, because he had used too thick-walled tubing. The great point was to have the external diameter as small as possible relatively to the bore. Jets of the size he had mentioned seemed to deliver quite as rapidly as one wanted. The papers mentioned by him in the *Lancet* on the subject of drop-measuring might be usefully studied in this connection. The author's suggestion was that drop-measurements might be used instead of loops for bacteriological cultures, and this had been found to be quite as easy as using graduated pipettes, especially when the divisions were so small as $\frac{1}{100}$ c.c.

Mr. W. T. BURGESS remarked that in drop-measurement the question of surface tension was of the utmost importance, and in the case of culture media, unless they were always of exactly the same composition, any attempt to measure definite quantities by drops would be hopeless. As an extreme instance of large alteration of surface tension by a minute admixture one might mention the case of saponin, of which a very small quantity, not affecting the specific gravity to an appreciable degree, would alter the surface tension of water enormously.

Mr. COSTE said that, as a rule, such methods would be used under reasonably ordinary conditions, and the fact that surface tension had an influence was, of course, well known, though its exact nature seemed from recent work to be rather doubtful.

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ERRATA.

1916.	Page	344,	five	lines	from	bottom,	171 should be 174.
,,	,,	383,	nine	,,	top,	1916 ,,	1911.
1917.	,,	197,	three	,,	,,	Co, 5·01 ,,	Co, 5·61.
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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Effects of Feeding Cottonseed Products on the Composition and Properties of Butter. C. M. Eckles and L. S. Palmer. (Missouri Agric. Exper. Station, *Bull.*, No. **27**, 1916; through *Int. Rev. Sci. Prac. Agric.*, 1917, **8**, 1021-1022.)—The feeding of cottonseed products effects a decrease in the Reichert-Meissl and saponification values of butter fat, whilst the iodine value and the melting-point of the fat are raised. The butter is rendered firmer and is of a better keeping quality. These effects are modified by the character of the raw foodstuffs which form the basis of the ration given to the cows. For example, the effects are most marked when dry hay and cottonseed products constitute the food, but a fairly large proportion of maize silage practically neutralises the effect of the cottonseed on the butter fat. The alteration in the Reichert-Meissl and iodine values is somewhat modified when the cows are fed continuously with cottonseed meal, but the effect on the melting-point of the butter fat remains the same as long as the meal is given to the animals.

W. P. S.

Fermentation of Philippine Cacao. H. C. Brill. (*Philippine J. Sci.*, 1917, **12**, 1-15.)—A full experimental and analytical study has been made of Criollo and Forastero cacao fermented under various conditions and for different lengths of time. It is concluded that the Philippine Islands can grow a good quality of cacao in large quantities, although at present little more is grown than is needed for local consumption. The preponderating weight of opinion is in favour of fermentation, although it is possible to prepare cacao without it. The enzymes found in the Criollo and in the Forastero types are identical in character, but exist in larger quantities and are more active in the former. In the fermenting bean were found casease, protease, oxidase, raffinase, diastase, invertase, and emulsin-like enzymes. The fermentation of the beans is spontaneous, and the methods of preparation are very crude. The average weight of the fruit and the percentage of the seeds in the Criollo variety is considerably greater than for the Forastero, due to a more careful selection of this variety for planting; the Forastero is much the more generally grown. In experimental fermentations in small quantities Criollo fermented more rapidly than the Forastero, a finer product being obtained, as judged by odour, colour, etc.

In the following table a comparison is made between the average values obtained for some twenty samples of fermented Philippine shelled cacao seeds with values found for beans from other districts.*

* Some of these are recorded by Ridenour (*Am. J. Pharm.*, 1895, **67**, 207).

All figures are given as percentages on the dry shelled seed.

	Bahia.	*Surinam.*	*Java.*	*Trinidad.*	*Aruba.*	*Caracao.*	*Granada.*	*Tabasco.*	*Machala.*	*Maracaibo.*	*Maximum.*	*Minimum.*	*Average.*	*Average for Philippine Criollo.*	*Average for Philippine Forastero.*
Fat	44·77	43·44	47·64	46·61	46·00	39·42	46·57	51·75	49·75	44·77	51·75	39·42	46·07	51·99	50·06
Theobromine	1·14	0·98	1·22	0·90	0·91	1·20	0·79	1·17	0·81	1·09	1·22	0·79	1·02	0·97	0·88
Albuminoids	7·97	10·82	9·76	12·70	10·77	11·33	10·31	7·98	13·45	12·25	13·45	7·98	10·73	12·15	13·24
Dextrose ..	1·13	1·33	1·30	1·47	0·44	2·94	1·91	0·95	1·70	1·15	2·94	0·44	1·45	0·46	0·27
Starch ..	8·01	3·81	5·45	5·32	1·67	4·08	6·61	3·57	1·43	1·79	8·01	1·43	4·17	5·24	4·89
Cane-sugar ..	0·54	0·37	0·54	0·34	6·76	1·67	0·58	2·76	0·49	1·44	6·76	0·34	1·45	0·51	0·98
Lignin ..	8·36	4·11	6·43	6·03	4·88	3·51	5·85	6·54	6·30	7·59	8·36	3·51	5·96	—	—
Cellulose ..	14·67	17·07	14·60	13·90	14·95	17·50	14·24	12·77	12·00	18·36	18·36	12·00	15·01	14·69	14·51
Extractive (by difference)	9·56	14·21	9·39	8·88	9·56	13·61	10·29	9·51	9·56	7·20	14·21	7·20	10·18	12·96*	14·41
Ash	3·83	3·21	3·49	3·84	3·96	4·66	2·86	3·11	4·40	4·38	4·66	2·86	3·78	4·99	4·78

* Extractive matter direct.

An examination of cacao butter was also made to determine what changes, if any, took place in it under different conditions of fermentation, the constants examined being saponification value, acid value, refractive index, also colour, and odour. The slight change in the acidity of the butter, coupled with the greater length of fermentation, confirms the author in his previous conclusion that Philippine cacao does not contain lipase. The changes brought about by fermentation are difficult to demonstrate by an analysis of the finished cacao, being chiefly characterised by an improvement in its organoleptic properties. The theobromine shows no regular variation, and there is no evidence that one of the results of fermentation, as claimed by Sack, is the splitting of a glucoside with the formation of theobromine and cacao-red. The sugar usually described as dextrose in the analysis of fermented cacao is, doubtless, largely maltose, the product of the action of diastase on the starch, which does not in itself undergo any decisive change in percentage amount during fermentation, although it is probable that a change takes place in its character, as evidenced by the so-called " break " of fermented cacao. The most obvious change which appears in the analytical data is the alteration in the percentage of astringent matter with length of fermentation, and here, again, the superiority of the Criollo variety is apparent.

Van Hall states (" Cacao," 1914, p. 201) that good cacao should show 12 per cent. or more of extractive matter, an amount slightly exceeded by the average Philippine product. Experiments were made in which seeds were sterilised to destroy the activity of the enzymes, yeast being subsequently added; but the final product was not satisfactory, and it would appear that yeasts alone do not produce the desired changes; the yeast employed for inoculation was that found growing on the cacao. Evidence is given for the belief that satisfactory cacao fermentation is the joint result of the action of yeasts and of enzymes. The enzymes already existing in the cacao alone would not appear to bring about all the desired changes, and would seem to need in addition the enzymes of yeasts, bacteria or moulds.

The superiority or the peculiarity of certain cacaos is probably largely due to the presence of certain yeasts or moulds, but the use of pure culture yeast is obviously impracticable. H. F. E. H.

NOTE BY ABSTRACTOR.—It will be noted that the values given for lignin and cellulose are very high. No definition of these substances is given, and the analytical methods employed are not described.

Estimation of the Alkalinity of Cacaos and Examination of Added Alkaline Materials. M. X. Rocques. (*Ann. Chim. anal.*, 1917, **22**, 201.)—French law (by a decree dated December 19, 1910, articles 17 and 18) permits the addition to cacao of alkalis or alkaline carbonates, provided the amount added does not exceed 5·75 per cent. of potassium carbonate or its equivalent in other alkali on the dry fat-free cacao matter. It is further stipulated that in cacaos to which no alkaline addition has been made the alkalinity calculated as potassium carbonate on the dry fat-free matter should not exceed 2·75 per cent., while cacaos to which alkali is added should not exceed 5·75 + 2·75—that is to say, 8·5 per cent. It has been shown, however, that many cacaos to which no alkaline addition has been made normally show an alkalinity in excess of 2·75 per cent., and the author recommends that there should always be determined total ash, ash soluble and insoluble in water, alkalinity of the soluble ash, and phosphoric acid in the soluble ash. With these data it is possible to determine whether or not the sample under examination is alkalised, and, if so, the amount added. A graph is given in the paper which shows at a glance the curve obtained for each of these values when the amount of potassium carbonate added ranges from 0 to 5 per cent. The titration of the ash should be carried out, using both tropæolin and phenolphthaleïn as indicators. It is found that the soluble ash increases as the insoluble diminishes, and the ratio $\frac{\text{insoluble ash}}{\text{soluble ash}}$ which is 2 for unalkalised cacao, will become less than unity in the case of alkalised samples. H. F. E. H.

Possibilities of Gulaman Dagat as a Substitute for Gelatin in Food. A. H. Wells. (*Philippine J. Sci.*, 1916, **11**, 267-271.)—Gulaman Dagat, a seaweed of the genus *Gracilaria* found throughout the Philippine Islands, was investigated as regards its food value and as a suitable substitute for gelatin. Experiments showed that it might serve as a substitute for gelatin where only the physical properties of gelatin are important, but that it is unsuitable for use in bacteriological work, owing to its low crushing pressure and slight surface strength. It somewhat resembles ordinary agar-agar, but has a less strongly marked solidifying power, does not melt so freely, and is not so fluid when melted and solidifies at a higher temperature. Gulaman Dagat differs chemically from gelatin in that it is not a protein; it contains less than 1 per cent. of nitrogen, and is as low in all nutritive substances. H. F. E. H.

Estimation of Fat in Certain Milk Products. C. K. Francis and D. G. Morgan. (*J. Ind. and Eng. Chem.*, 1917, **9**, 861-862.)—For the estimation of fat in

powders and semi-liquid preparations such as ice-cream a modification of the Babcock test is recommended, in which the sulphuric acid is replaced by mixtures of sulphuric, nitric, and acetic acids, with the object of preventing excessive carbonisation of carbohydrates. *Ice-Cream and Evaporated Milk.*—Ten c.c. of the melted and uniformly mixed ice-cream are withdrawn with a pipette, and 9 grms. rapidly weighed into a 30 per cent. cream test bottle; or in the case of evaporated milk 4·5 grms. of the dry powder, or 9 grms. if in diluted form, are used. The sample is treated with a mixture in equal parts of glacial acetic and sulphuric acids, which is added 4 to 5 c.c. at a time, until a dark brown colour develops. Concentrated nitric acid is then added, 1 to 2 drops at a time, with shaking after each addition, until the colour becomes light yellow, when the bottle is immersed in boiling water for three to four minutes until the brown colour reappears. It is then centrifuged for five minutes at 1,200 r.p.m., hot water introduced, so as nearly to fill the neck, and the centrifuging continued for two minutes, when more hot water is added to bring the column of fat into the neck. After a final centrifuging for one minute, glymol is added to reduce the meniscus, and the reading taken. *Malted Milk.*—The sample (4·5 grms.) is treated with a mixture of 20 c.c. of sulphuric acid and 1 c.c. of nitric acid, of which 1 to 1·5 c.c. is added at a time, with shaking after each addition, until a light yellow coloration is obtained. The bottle is immersed in boiling water until its contents turn dark brown, and a mixture of 10 c.c. sulphuric acid with 2·5 c.c. of nitric acid is then introduced, 1 c.c. at a time, with shaking after each addition, until the colour appears light red and has begun to darken. The bottle is now immersed again in boiling water until the dark brown colour returns, when it is centrifuged for five minutes, hot water added, and the centrifuging repeated for two minutes, and then, after the addition of more hot water, for one minute, as described. *Dried Milk.*—The sample (4·5 grms.) is treated with strong sulphuric acid, 5 to 6 c.c. at a time, until a very dark brown colour is obtained. It is then treated with a mixture of 10 c.c. of sulphuric acid with 2·5 c.c. of nitric acid, 0·5 c.c. at a time, with thorough shaking after each addition, until a light red colour appears, when the bottle is immersed in boiling water until the dark brown colour returns. More of the acid mixture is then added to restore the light red colour, and the bottle again immersed in boiling water until the contents are brown again, when it is centrifuged as described for malted milk. C. A. M.

Cryoscopic Method for Estimating Added Water in Milk. J. T. Keister. (*J. Ind. and Eng. Chem.*, 1917, **9**, 862-864.)—From 15 to 20 c.c. of the milk, previously cooled nearly to the freezing-point, are placed in a tube about 19 cm. long by 22 mm. in diameter and 1·5 mm. thick; the upper length of about 3·5 cm. is widened to 30 mm. diameter, so as to take a stopper through which is passed the Beckmann thermometer and a wire stirrer. This tube is fitted into a large test-tube, a piece of rubber-tubing being used to make a tight joint at the shoulder. The double tube containing the milk is lowered into a freezing mixture of 40 to 50 grms. of salt and 900 to 1,000 grms. of ice shavings, so that the whole of the milk is below the surface of the freezing-bath. When the thermometer is about 1° C. below the true freezing-point, the sample is gently stirred to break up ice particles, and the highest

rise of temperature noted. The operation is repeated two or three times, and the freezing-point of recently boiled distilled water is also determined in the same way. The difference between the readings obtained with the milk and the water gives the freezing-point of the sample. The results thus obtained with samples of milk from sixteen different cows showed that 5 per cent. of added water could be detected in most cases, and that in any case they gave rise to suspicion. Any addition of water in excess of 5 per cent. may be detected with certainty. The effect of formaldehyde in sufficient quantity to preserve milk is to depress the freezing-point. The test is only applicable to fairly fresh milk, since an increase of 0·1 per cent. of acidity beyond the normal acidity of 0·15 per cent. counterbalances the depression of the freezing-point caused by the addition of about 5 per cent. of water. (See ANALYST, 1915, **40**, 55.)

Titration and Estimation of Morphine with Iodic Acid. J. N. Rakshit. (*J. Soc. Chem. Ind.*, 1917, **36**, 989-990.)—In dilute sulphuric acid solution morphine is oxidised quantitatively, two molecules of morphine absorbing three atoms of oxygen. For the titration, from 0·05 to 0·15 grm. of the alkaloid is dissolved in 50 c.c. of water, and 5 c.c. of $\frac{N}{10}$ sulphuric acid and 10 c.c. of 1 per cent. freshly prepared starch solution are added, followed by 15 c.c. of $\frac{N}{5}$ iodic acid solution; the mixture is shaken, kept in a dark place for fifteen minutes, and then titrated with $\frac{N}{10}$ thiosulphate solution. The number of c.c. of $\frac{N}{5}$ iodic acid solution used for the oxidation is multiplied by 0·0190 to obtain the quantity of morphine present. The end-point of the titration is denoted when the blue coloration has remained discharged for at least thirty seconds. The results obtained are trustworthy, but the reaction cannot be used for the estimation of morphine in opium, since codeine, narcotine, and other substances contained in opium absorb oxygen. The reduction of iodic acid by an excess of morphine is incomplete. W. P. S.

By-products of Rice Milling. J. B. Reed and F. W. Liepsner. (*Bull.* No. 570, Bureau of Chem., U.S.A. Dept. Agriculture, August 11, 1917.)—The three varieties of rice most grown in the United States are the Japan, Honduras, and "Blue Rose" type, the first of which has a short, thick grain, and the second a long kernel, whilst the last type is intermediate between the other two in size. After screening and cleansing, the cleaned rough rice is crushed between hulling stones, and passed through the meshes of a "stone reel," which separates the broken hulls, germs, and true bran, the mixture of which is termed "stone-reel bran." The rice and hulls passing over the screens are next shaken in the "paddy machine," which separates the rough from the hulled rice, and the former or "paddy" grains are passed through hulling stones more closely set than the first pair, and re-enter the stream going towards the stone reel. The natural brown rice from the "paddy machine" is next treated in "first-class hullers," which remove the bran layers from the hulled grain, and the loosened bran is separated by means of the "first-break reel" and constitutes the "first-break" bran, whilst the rice is again treated in hullers more closely set, and in a reel which separates the "second-break bran." In some mills the bran is removed more gradually by means of a machine termed a

"pearling cone." The rice from the hullers or pearling cone is passed through a brush machine, where it is polished over a screen by means of brushes which remove more of the inner bran coat, and the screenings from this machine constitute the commercial "rice polish." The following table gives the average analyses of these various by-products from about twenty different mills:

By-product.	Moisture.	Ash.	Ash Insoluble in 10 % HCl.	Ratio of Insoluble Ash to Total Ash.	Crude Fibre.	Protein, N × 6·25.	Ether Extract.
Rice hulls:	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Maximum	9·69	22·03	20·98	—	46·82	4·12	1·31
Minimum	5·00	16·40	15·27	—	36·57	1·75	0·51
Average	7·93	19·54	18·58	1 : 1·05	41·29	2·66	0·80
Stone-reel brans:							
Maximum	17·31	19·29	16·85	—	26·49	12·86	13·54
Minimum	6·75	10·80	6·19	—	9·40	7·49	5·15
Average	10·19	14·97	11·28	1 : 1·33	19·38	10·21	8·28
Huller brans and pearling-cone meals:							
Maximum	13·67	10·38	3·37	—	10·70	18·64	20·61
Minimum	6·83	4·63	0·17	—	1·41	10·71	8·52
Average	9·45	8·02	1·29	1 : 6·22	7·31	14·72	16·30
Mixed brans as sold by the mill:							
Maximum	15·00	13·38	6·44	—	12·96	16·65	17·49
Minimum	7·78	7·85	2·24	—	9·54	11·88	9·74
Average	9·65	10·03	3·78	1 : 3·77	11·28	13·79	14·75
Rice polishes:							
Maximum	13·03	9·61	1·40	—	3·67	15·24	13·68
Minimum	5·64	2·07	0·24	—	0·56	7·87	6·29
Average	9·45	4·97	0·64	1 : 7·76	2·07	12·11	9·75

The stone-reel brans usually contain from 25 to 50 per cent. of hulls, which accounts for their containing more ash and fibre and less protein and fat than the huller brans. The latter, although suitable as feeding stuffs, do not keep well, and in practice are blended with the product from the stone reel to form the commercial bran. This should contain more than 26 per cent. of fat and protein together, and should not contain more than 13 per cent. of crude fibre or 5 per cent. of ash insoluble in hydrochloric acid. The presence of rice hulls in rice bran is shown by the high ash —especially insoluble ash (silica)—by a low ratio of insoluble ash to total ash, and a high percentage of crude fibre. The composition of the rice hulls is such that they have but little food value, whilst their physical structure renders them injurious to animals if given in large amounts. C. A. M.

Occurrence and Significance of Mannitol in Silage. A. W. Dox and G. P. Plaisance. (*J. Amer. Chem. Soc.*, 1917, **39**, 2078-2087.)—Of the various isomeric hexatomic alcohols occurring in nature, mannitol is by far the most abundant, and

is a normal constituent of maize silage and of silage made from other plants containing cane-sugar. Mannitol is produced in silage fermentation by bacterial reduction of the lævulose half of the cane-sugar molecule. At the same time the characteristic constituents of silage—acetic acid, lactic acid, carbon dioxide, and alcohol—are also formed, while part of the mannitol disappears. Storer's test for mannitol, which consists in oxidation to mannose and precipitation of the latter as the phenylhydrazone, is qualitative only, since a part of the mannitol escapes conversion into mannose. The authors therefore effect its isolation by direct crystallisation, taking advantage of the fact that mannitol is readily soluble in hot alcohol, but only sparingly so in cold. The alcoholic extract of the material under investigation is evaporated, and on standing over-night a mass of mannitol crystals forms, which on further purification crystallise in snow-white needles (m.-p. 169° C.). The separation of magnesium lactate is prevented by the addition of a small quantity of hydrochloric acid. The amount found in normal maize silage varies from nil to 5·6 per cent., while cane and sunflower silage contain mannitol greatly in excess of this amount. These two plants contain a higher percentage of cane-sugar than maize, whereas sweet clover, which yields no mannitol on fermentation, contains little, if any, cane-sugar. Other workers have found that *Bacillus manniticus* produces mannitol from invert sugar and lævulose, but not from dextrose, galactose, mannose, sorbose, maltose, or lactose. That the formation of mannitol is due largely, if not wholly, to the action of micro-organisms rather than that of the plant enzymes was shown by an experiment in which no formation of mannitol was observed subsequent to sterilisation unless the whole were inoculated with a decoction from a leaf of maize silage. It is also shown that no mannitol is formed in any case unless cane-sugar, or lævulose itself, is present. Estimations of mannitol in silage showed that there was an increase in the amount present in silage up to the twelfth day, after which it rapidly decreased in amount, owing to bacterial action, and it is probable that its presence accounts in large measure for the deficit noted when the sum of the other ordinary fermentation products is balanced with the original sugar fermented. It is shown that mannitol can be recovered from commercial silage without detriment to the nutritive value of this material, and it is suggested that a useful explosive could be prepared from it, since it yields a nitration product very similar in properties to nitro-glycerine (see Sanford, "Nitro-Explosives," 1906, p. 110).

H. F. E. H.

Occurrence of *l*-Leucine in Sweet Clover Silage. G. P. Plaisance. (*J. Amer. Chem. Soc.*, 1917, **39**, 2087-2088.)—Unlike the other legumes, such as alfalfa and clover, sweet clover (*Melliotus alba*) can be made into silage without the addition of other plants to supply fermentable sugar. On being subjected to the author's process for the isolation of mannitol (see preceding abstract), no evidence whatever of this substance was found, but instead a white substance crystallised in small round masses, which on recrystallisation from dilute alcohol was obtained in snow-white, flat, scaly crystals. It proved on analysis to be leucine, and was further identified by its specific rotation and by the properties of its benzoyl derivatives. In the samples of sweet clover silage examined the amount of leucine recovered

ranged from 0·4 to 1 per cent. of the dry material. Its occurrence in silage has not been previously reported. H. F. E. H.

Tables for the Analysis of Food Substances containing Sugar. Syrups, Sweets, Honey, etc. H. Lajoux and L. Ronnet. (*J. Pharm. Chim.*, 1917, **16**, 199-204.)—The following table is given for the purpose of simplifying analyses of these products and in order that the results obtained may be seen at a glance. A solution (ϵ) is prepared by dissolving a known quantity or volume of the substance in water and diluting the solution, after clarification, so that it shall contain from 5 to 10 grms. of sugar. For the estimation of the copper-reducing power, a portion of this solution is further diluted so that a given volume of it shall reduce approximately the same volume of Fehling's solution; let this solution be called σ.

	In 100 c.c. of Solution ϵ.
Solution ϵ: Q grms. or V c.c. of substance in 100 c.c. Solution ϵ, inverted: Q grms. or V c.c. of substance in 110 c.c.	Cane-sugar, $S = \dfrac{95D}{176{\cdot}75 - 0{\cdot}56t} = D \times K$.
Solution σ: v c.c. of solution ϵ in 100 c.c.	Reducing sugars, $R = \dfrac{10{\cdot}000q}{N \times v}$.
Dextrin solution: Dextrin from 100 c.c. of solution ϵ in 100 c.c. Fehling solution: 10 c.c. correspond with q grms. invert sugar.	Dextrose, $G = \dfrac{50A + R(103{\cdot}4 - 0{\cdot}56t) - 66{\cdot}5S}{156{\cdot}4 - 0{\cdot}56t}$ In the presence of dextrin, A is replaced by $A - a$.
Solution ϵ: Rotation in 20 cm. tube at $t° = A$. Solution ϵ, inverted: Rotation in 22 cm. tube at $t° = A'$. Difference: $D = A - A'$.	Lævulose, $L = R - G$.
	Dextrose in excess, $g = G - L$. Lævulose in excess, $l = L - G$.
Solution σ: 10 c.c. of Fehling's solution reduced by N c.c. Dextrin solution: Rotation in 20 cm. tube at $t° = a$.	Invert sugar, $I = 2L$ or $2G$, according to which is the smaller.
Dextrin solution, saccharified: $\dfrac{100}{110}$; 100 c.c. of Fehling's solution reduced by n c.c.	Dextrin, $\Delta = \dfrac{99 \times q}{n}$.

The dextrin is obtained by evaporating a portion of solution ϵ to a syrupy consistence, adding 3 c.c. of concentrated hydrochloric acid and 100 c.c. of alcohol, and collecting the precipitate on a filter; the precipitate is then dissolved in 3 c.c. of hydrochloric acid, again precipitated with alcohol, collected, and dissolved in water in quantity equal to that of the solution taken originally. If dextrin is present,

this solution will be strongly dextro-rotatory. The dextrin is converted into dextrose by boiling 50 c.c. of the solution with 0·5 c.c. of hydrochloric acid for three hours under a reflux condenser. W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Detection of Mercury in Toxicological Cases. C. L. Spica. (*Gazz. Chim. Ital.*, 1917, **47**, 139-144.)—A series of experiments was made to determine whether mercuric chloride and calomel undergo material change when kept in contact with visceral material preserved with alcohol, as is usually done. Two portions of about 200 grms. of the fresh material were immersed in 95 per cent. alcohol, and 1 c.c. of a 4 per cent. aqueous solution of mercuric chloride was added to one portion, and 0·5 grm. of pure calomel to the other. The closed flasks were then left for two years exposed to diffused daylight. The alcoholic liquid was then drained off and the residue washed with water, and then successively extracted with 10 per cent. hydrochloric acid and 10 per cent. nitric acid, being washed after each extraction. Finally the mass was decomposed with hydrochloric acid and potassium chlorate, as in the Fresenius-Babo process. Tests for mercury were applied to each of the extracts thus obtained, and from the results the following conclusions were drawn: (1) Mercuric chloride left in contact with visceral material and dilute alcohol is partially converted into a form (probably an albuminate) which is not extracted by dilute hydrochloric acid; but only a very small proportion is converted into a compound which is not extracted by successive treatment with dilute hydrochloric acid or nitric acid or rendered soluble by the simultaneous action of hydrochloric acid and potassium chlorate. (2) It is doubtful whether under the conditions described any calomel would be converted into a form soluble in dilute alcohol. (3) It has been proved that a considerable amount of calomel, left under the conditions described, is converted into a compound (probably albuminate) which is soluble in dilute hydrochloric acid, and most of which can be separated as metallic mercury by simple electrolysis of the solution. C. A. M.

Methods for the Estimation of Metabolic Nitrogen. E. B. Forbes, C. E. Mangels and L. E. Morgan. (*J. Agric. Research*, 1917, **9**, 405-411.)—The so-called metabolic nitrogen of fæces is that portion which has an origin other than as indigested food residue. It consists of residues from the bile and digestive juices, epithelium and mucus from the digestive tract, and of such products of bacterial activity as have been derived from digested or from digestible nitrogen. It is evident that it is necessary to know the amount of this metabolic nitrogen in fæces in order to judge of the digestibility of any proteins in animal or human nutrition experiments. The methods compared in this study were the acid-pepsin method, the acid-pepsin and alkaline-pancreatin method, and the alcohol-ether, hot water, and cold-lime water method of Jordan (*Maine Agric. Exp. Sta. Ann. Rpt.*, 1888, 197).

By the first two methods it is assumed that the nitrogen which has been digested, absorbed, and returned to the fæces is separated from the indigestible nitrogen, and

that there is no further digestion during the course of the estimation of that part of the food protein which escaped digestion in the alimentary tract. There are no means of proving the truth of this latter assumption. The acid-pepsin plus alkaline-pancreatin method more nearly follows the physiological process, since intestinal digestion is also represented; it yields decidedly higher results. In the Jordan method the treatment with the solvents selected is designed especially for the purpose of washing out bile residues, protein cleavage products and mucin. The plan of the experiments was to feed a basal ration of maize alone to pigs during the first period, and to add to this corn ration in subsequent periods nitrogenous supplements to be used in the comparison of methods. These supplementary substances—milk, blood albumen, and commercial dried egg albumen—were chosen as containing proteins which would probably be entirely digestible, and the effort was made to determine which of the three methods above alluded to would assign to such protein a digestion coefficient equal to 100 per cent. The apparent digestibility of the protein of maize based on the total nitrogen of the fæces is about 75 per cent., but since some of the nitrogen in the fæces is of metabolic origin the real digestibility must be higher. The acid-pepsin method makes it appear that the real digestibility of maize protein is about 92 per cent., and the pepsin-pancreatin method about 96 per cent.; Jordan's method averages only 86 per cent. The acid-pepsin method indicates that 70 per cent. of the nitrogen of the fæces from maize is of metabolic origin, the pepsin-pancreatin method showing 84 per cent., and the Jordan method 46 per cent. All the methods make the nitrogen of blood albumen appear more than completely digestible, even the apparent digestibility being over 100 per cent.; thus the feeding of blood albumen with maize seems to increase the digestibility of the maize protein to an extent more than sufficient to offset the incompleteness of digestibility (if any) of the protein of this supplement. It would also appear that raw commercial dried egg albumen is almost perfectly digested by swine. The digestion coefficients for protein involved in the feeding standards found in reference works on animal production assume that the nitrogen of the fæces is entirely an indigestible food residue. Such an assumption would appear to underestimate the digestibility of proteins by about 20 per cent. It is evident that the acid-pepsin and the pepsin-pancreatin methods give results which are more nearly true than does Jordan's method, since the latter does not digest the fæcal bacteria, which may contain large proportions of the nitrogen of the fæces, and such fæcal bacteria are presumably more largely the product of digestible than of indigestible protein. The author concludes that there is no really accurate scientific basis for the determination of the digestibility of protein. H. F. E. H.

ORGANIC ANALYSIS.

Relations in Composition of the Different Forms of Natural Bitumens. C. F. Mabery. (*J. Amer. Chem. Soc.*, 1917, **39**, 2015-2027.)—Bituminous coal from Deerfield (Ohio) yields, by distillation under reduced pressure, a number of hydrocarbons, mostly of the series C_nH_{2n-4}, resembling the hydrocarbons that compose the neighbouring Mahone petroleum. Utah Gilsonite gives members of the series

C_nH_{2n} and C_nH_{2n-2}, that resemble the same hydrocarbons in petroleum, also a series of unsaturated hydrocarbons. It contains in large proportion the nitrogen compounds that are found in all petroleum, which demonstrates its organic origin. Grahamite gives a series of hydrocarbons resembling those from Gilsonite.

G. C. J.

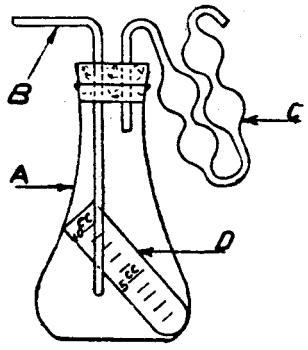
Duclaux Method for the Estimation of Volatile Acids. L. J. Gillespie and E. H. Walters. (*J. Amer. Chem. Soc.*, 1917, **39**, 2027-2055.)—Many of the difficulties experienced in the practical application of the Duclaux method have been due to the lack of suitable procedure for calculating the results, and the present paper consists of a long and critical examination of the mathematical methods involved. The distillation of the dilute acid solutions is affected by electrical heating, bare nichrome wire being employed. A volume of 110 c.c. is always employed, and ten lots of 10 c.c. are collected for titration. It was found that for the determination of the constants specially pure acids were unnecessary, and values are given for formic, acetic, propionic, and butyric acids. The laws which must be assumed in order to calculate the results of analyses by the Duclaux method are stated and verified; both algebraic and graphic methods for the computation of the results of mixtures of two or of three acids are described, and the algebraic calculation for four or more acids is indicated. Application of the method to known mixtures shows that mixtures of two or of three acids may be quantitatively analysed without too great error by either algebraic or graphic methods, but, in general, the errors are too large for mixtures of four acids. It is shown that the errors of the method are not proportional to the quantities of acid present, while if four or more acids are present in significant quantities the mixture must be fractionated, before distillation, into mixtures containing only three acids in significant quantity. In order to apply the Duclaux method to unknown mixtures, it is necessary to establish that not more than three acids are present in significant quantities; this being established, a distillation by the Duclaux method should suffice for both the qualitative and quantitative analyses of the mixture. The methods of calculation are not in conformity with the laws governing the rates of distillation of pure acids in aqueous solution, and do not therefore necessarily depend on the mode of distillation. The calculations may therefore be applied to distillations made in other ways—for instance, to steam distillations at constant volume; it is merely necessary to conduct all distillations both of pure acids and of mixtures in the same manner. (*Cf* ANALYST, 1917, 149 and 214.) H. F. E. H.

Estimation of Halogens in Organic Compounds. J. F. Lemp and H. J. Broderson. (*J. Amer. Chem. Soc.*, 1917, **39**, 2069-2074.)—The method recommended is that of Parr (*Amer. Chem. J.*, 1904, **41**, 386) by fusion with sodium peroxide, but, instead of Parr's bomb, the authors use a special fusion cup made for them by the Standard Calorimeter Company, East Moline, Ill. The sodium peroxide (10 grms.) is first mixed with 1 grm. of potassium nitrate, then with 0·5 grm. of cane-sugar, and finally with the sample (0·2 to 0·25 grm.). Liquids are weighed out in small sealed glass bulbs which are broken by tapping the bomb on the table. Ignition

is effected by heating the cup in the hottest part of a Bunsen flame, heating being continued until a quarter of the cup is red hot. The bomb is immediately quenched under the tap, opened, and the contents treated with 200 c.c. of water, which is subsequently boiled to decompose peroxide. Excess of standard silver nitrate solution is added to the alkaline solution, which is digested for fifteen minutes before acidifying with nitric acid. This avoids loss of iodine. Finally, hydrazine sulphate is added slowly, to reduce iodate to iodide. When frothing ceases, sufficient has been added. The excess of silver is then estimated by Volhard's method, and the silver halide calculated. G. C. J.

Estimation of Silver in Organic Compounds. H. J. Lucas and A. R. Kemp. (*J. Amer. Chem. Soc.*, 1917, **39**, 2074-2078.)—The cyanide-sulphide method is recommended. The sample (0·3 grm.) is dissolved in $\frac{N}{4}$ sodium cyanide, of which 2 or 3 drops are added in excess. The solution is warmed and, as soon as the solid has dissolved, 10 c.c. of $\frac{N}{1}$ sodium hydroxide are added, and the solution diluted to 300 c.c. About 25 c.c. of $\frac{N}{4}$ sodium sulphide in excess of the theoretical amount required for the precipitation of the silver are added slowly with stirring, and the solution is heated to 60° C. and stirred until the precipitate has coagulated. The precipitate is then filtered off on a Gooch crucible, washed with water until free from soluble sulphide, then with alcohol and ether, and dried at 100° to 110° C. for half an hour. The excess of sodium sulphide mentioned ensures the precipitation of all but 0·05 mgrm. of silver. The method has not yet been applied to salts containing nitrogen and sulphur. It is not applicable to salts which are insoluble in excess of cyanide solution, and will probably not work satisfactorily with those salts the acids of which form insoluble sodium or potassium salts, or the acid radicals of which contain easily reducable nitro-groups. In a number of cases in which it was tried it gave excellent results. G. C. J.

Estimation of Nitrogen in Explosives. B. Oddo. (*Gazz. Chim. Ital.*, 1917, **47**, 145-158.)—The nitrogen in explosives may be conveniently estimated by means of a gravimetric nitrometer of the form shown in the diagram. It consists of a flask, *A*, of about 100 c.c. capacity, closed by a stopper through which pass the tube *B* and the end of a bulb tube, *C*, which is intended to act as a sulphuric acid valve. The weighed quantity of the explosive is introduced into the flask, together with some sulphuric acid, and then the tube *D*, in which has been placed mercury in excess of that corresponding to the weight of sulphuric acid. A little sulphuric acid is drawn up into the tube *C*, so as to form a seal in the lowest bend, the end of the tube is connected with a beaker containing sulphuric acid, and dry carbon dioxide is aspirated through the apparatus for forty to forty-five minutes, until all air has been removed from the sample. The rubber tube is then disconnected from *C*, the inlet and outlet of the tubes closed with corks, and the



apparatus is weighed. The tube *C* is next opened and connected with the beaker of acid again, and the flask inclined so as to cause the mercury to fall out of the tube *D*. The flask is gently shaken with a circular movement, and eventually warmed and shaken more vigorously to promote the separation of the nitric oxide, and finally a current of dry carbon dioxide is swept through the apparatus as before, the tubes corked, and the loss in weight determined. From the amount of nitric oxide thus estimated by difference the percentage of nitrogen is calculated. The method gives results in close agreement with those obtained with the ordinary nitrometer. In practice several of these flasks may be connected with the apparatus supplying the current of dry carbon dioxide. C. A. M.

Thermal Values of Oils and Fats. II. The Maumené Value. J. W. Marden and M. V. Dover. (*J. Ind. and Eng. Chem.*, 1917, **9**, 858-860.)—By means of apparatus similar to that used in determining the bromine thermal value (ANALYST, 1916, **41**, 176) the Maumené value may be expressed in calories per grm. of oil. Provided the same weights of acid, oil, and water be used, the heat capacity of the system may be regarded as constant. A Dewar vacuum-tube is used as the calorimeter vessel, and is standardised by measuring the heat evolved on diluting sulphuric acid of definite strength with water. The Maumené value in calories per grm. is found by multiplying the observed rise of temperature by the heat capacity of the system, and dividing the result by the weight of oil. The constancy of the results depends largely upon the strength of the acid, but a variation in the amount of acid has but little effect upon the value (*cf.* Mitchell, ANALYST, 1901, **26**, 169). C. A. M.

Analysis of Sulphonated Oils. R. Hart. (*J. Ind. and Eng. Chem.*, 1917, **9**, 850-852.)—The following rapid method of analysis is based upon the fact that Turkey-red oils and similar products can be practically completely saponified by heating with alcoholic alkali. *Estimation of Fat.*—A solution of the oil is titrated with $\frac{N}{2}$ sulphuric acid, using methyl orange as indicator, and the alkalinity is expressed in mgrms. of potassium hydroxides per grm. Another portion of the sample is used for the determination of the saponification value in the usual way, by boiling for forty-five minutes with $\frac{N}{2}$ alcoholic sodium hydroxide solution. The sum of the two results divided by the acid value of the original castor oil fatty acids gives the percentage of fat. In cases where the acid value is not known it is assumed that the fatty acids have the average value 190. The alkalinity required for calculating the amount of fat must be that which corresponds to the sodium (or potassium) soaps, and in determining the saponification value allowance must be made for the fat corresponding to any ammonium soap present, since the latter behaves like fatty acids during the saponification. For this purpose the solution is heated with a measured amount of standard sodium hydroxide solution, boiled to expel ammonia, and titrated with $\frac{N}{2}$ sulphuric acid, using methyl orange as indicator. *Ammonia.*—The alkalinity is estimated in one portion of the sample, as just described, whilst in the second portion it is estimated in the same way, except that the boiling with sodium hydroxide is omitted. The difference between the two results gives the

ammonia. *Sulphuric Anhydride.*—The oil is boiled with a measured quantity of standard sulphuric acid until completely decomposed, and is then neutralised with standard alkali, using methyl orange as indicator. During the boiling the following decomposition occurs:

$$2NaSO_3OC_{17}H_{32}CO_2Na + H_2SO_4 + 2H_2O = Na_2SO_4 + 2NaHSO_4 + 2HOC_{17}H_{32}CO_2H.$$

The original alkalinity is thus decreased by the formation of sodium sulphate, but increased by the sodium bisulphate, and the net change in acidity, which is given by the titration, is equal to the difference between the total alkalinity due to the soap and the acidity due to the sodium bisulphate. The total alkalinity is obtained as described above, and from these data the acidity corresponding to the sodium bisulphate. The results thus obtained in test experiments agreed closely with those obtained by the older standard methods and with the theoretical composition of samples prepared in the laboratory. C. A. M.

INORGANIC ANALYSIS.

Qualitative Separation and Detection of Gallium. P. E. Browning and L. E. Porter. (*Amer. J. Sci.*, 1917, **44**, 221-224, through *J. Soc. Chem. Ind.*, 1917, **36**, 1109.)—In the ordinary course of analysis gallium appears in the group containing aluminium, beryllium, chromium, and vanadium, from which group the last two elements may be removed by oxidation to the acidic condition and treatment of the solution with ammonia. Potassium ferrocyanide may be used for the separation of gallium from the remaining elements of the group, the separation from aluminium being the more important, since beryllium is seldom present in products containing gallium. The method depends on the insolubility of gallium ferrocyanide in hydrochloric acid; and, in a series of trials, each made in a volume of 5 to 10 c.c., of which from one-quarter to one-third was strong hydrochloric acid, 0·001 grm. Ga was precipitated at once by the addition of potassium ferrocyanide, whereas 9·1 grms. Al or Be gave no precipitate. Under similar conditions a precipitate was obtained with 0·0001 grm. Ga after standing for an hour. The test is vitiated by the presence of traces of zinc, but the latter may be removed by addition of hydrogen sulphide to the sodium hydroxide solution of the metals. The zinc sulphide is filtered off and the filtrate acidified, boiled to remove hydrogen sulphide, and then made alkaline with sodium hydroxide and treated with hydrogen peroxide in order to oxidise the free sulphur. The liquid is then boiled to decompose the excess of hydrogen peroxide, and acidified with hydrochloric acid and treated with potassium ferrocyanide. By this means it was found possible to detect 0·0002 grm. Ga in the presence of 0·05 grm. Zn. The most satisfactory method of decomposing gallium ferrocyanide and recovering the metal as hydroxide is to fuse the compound with ammonium nitrate and treat the residue with sodium hydroxide; a solution of gallium is thus obtained from which the hydroxide is precipitated on boiling with excess of ammonium chloride. The ether process for the separation of aluminium and iron chlorides is also applicable to the separation of aluminium from gallium, the latter being obtained as chloride in ethereal solution; in this way, 0·0005 grm. Ga was detected in the presence of 0·1 grm. Al, the ethereal

solution being evaporated to dryness and the residue dissolved in hydrochloric acid before the addition of potassium ferrocyanide. Subsequent experiments showed the precipitation of gallium ferrocyanide to be partly or wholly prevented by the presence of nitrates or nitric acid, but that these could be successfully removed by evaporation with hydrochloric acid.

Sensitive Reaction for Hydrogen Peroxide. G. Denigès. (*Ann. Chim. anal.*, 1917, **22**, 193.)—Fenton has shown that tartaric acid added to hydrogen peroxide in presence of a ferrous salt as catalyst produces, on the addition of caustic alkali, a violet coloration, due to the formation of a ferric compound of dioxytartaric acid. Investigation by the author showed that while not an altogether satisfactory reaction for the detection of tartaric acid, it was under certain conditions capable of revealing very small traces of hydrogen peroxide. Two c.c. of 5 per cent. tartaric acid solution and 1 or 2 drops of ferrous ammonium sulphate of the same strength are placed in a test-tube, and, after shaking, 1 or 2 drops of hydrogen peroxide are added; or, if the peroxide is highly diluted, as much as 2 c.c. may be added. After shaking and making alkaline with sodium hydroxide a violet coloration develops in the presence of as little as 0·04 to 0·05 of a mgrm. of oxygen.

H. F. E. H.

Blacher Method for the Estimation of Hardness in Water. A. S. Behrman. (*Philippine J. Sci.*, 1916, **11**, 291-293.)—Philippine waters contain large amounts of free carbonic acid and sodium chloride, and their effect upon the Blacher method has been investigated by the author. Aspiration of the sample for five or ten minutes will reduce the carbon dioxide to below 25 parts per million—a figure at which satisfactory results are to be obtained. Sodium chloride up to 2,000 parts of chlorine per million does not perceptibly affect the end-point of the titration. If the total hardness (as calcium carbonate) is much over 250 parts per million, it is advisable to dilute the sample with distilled water. For the titration $\frac{N}{10}$ potassium palmitate solution is prepared, according to the method given by Herbig (*Farb. Zeit.*, 1913, **24**, 113-114) for potassium stearate by the neutralisation of palmitic acid in alcoholic glycerol solution which is standardised against a saturated solution of calcium hydroxide. The acidity of the sample (due to free carbon dioxide) is first determined with sodium carbonate in the presence of phenolphthaleïn. The solution is then titrated with $\frac{N}{10}$ sulphuric acid, using 1 drop of dimethylamidoazobenzene (butter yellow) as indicator, to obtain the "bicarbonate alkalinity," which may be taken as a measure of the temporary hardness, in both cases making proper allowance for the normal carbonates. A few drops of $\frac{N}{10}$ sulphuric acid are added in excess, and the solution is aspirated for five minutes. Phenolphthaleïn is then added, followed by $\frac{N}{10}$ alcoholic potassium hydroxide until a slight pink coloration is produced in the yellow liquid. Titration is then made with $\frac{N}{10}$ potassium palmitate solution, the end-point not being taken at the first faint pink which is observed, at the first intense pink. This gives the total hardness as calcium carbonate in parts per million. If desired, the calcium may be separately determined and the magnesium obtained by difference. H. F. E. H.

Separation of Tin and Tungsten in Stanniferous Wolfram. Travers. (*Compt. rend.*, 1917, **165**, 408-410.)—The finely divided mineral is attacked by fusion with anhydrous sodium sulphite. The fused mass is disintegrated by treatment with boiling water, and the solution diluted to about 750 c.c. It is then neutralised, and a small excess of acid, not exceeding 20 c.c. of normal acid, is added. The brown stannous sulphide, contaminated by traces of silica, iron, and manganese, but free from tungsten, is filtered off and purified by solution in yellow ammonium sulphide and reprecipitation. The resulting yellow stannic sulphide is filtered off and ignited to oxide.

Tungsten is estimated in a separate sample, which is fused as above described, the fused mass being taken up directly in *aqua regia*. The bulk of the tungsten separates at once, with some silica, and is filtered off, the rest being recovered from the filtrate by co-precipitating it with ferric hydroxide. The mineral usually contains enough iron for the purpose, but in its absence ferric chloride corresponding to 10 per cent. of the weight of the sample is added. Ammonia is added in amount sufficient to precipitate the iron, but without making the solution alkaline to litmus. The precipitate, which contains practically the last of the tungsten, is washed and dissolved on the filter with hot dilute (1 : 1) hydrochloric acid. The solution is evaporated to dryness and the residue taken up in hydrochloric acid. The residue of tungstic acid, which retains less than 0·2 mgrm. of ferric oxide, is filtered off and,with the principal precipitate, freed from silica in the usual manner. The liquors may be tested colorimetrically for unprecipitated tungsten by means of titanous chloride, and the colorimetric test made quantitative if a positive reaction is found. The method is said to estimate tungsten with an error not exceeding 0·2 per cent. G. C. J.

APPARATUS, ETC.

Simplified Micro-Combustion Method for Determination of Carbon and Hydrogen. L. E. Wise. (*J. Amer. Chem. Soc.*, 1917, **39**, 2055-2068.)—The method is a modification of that of Pregl (Abderhalden's *Handbuch der Biochemischen Arbeitsmethoden*, [ii.], **5**, 1307), who used a Kuhlmann microbalance, now unobtainable outside Germany. The author's first modification, therefore, is the use of a balance sensitive only to 0·03 mgrm., and of 20 mgrms. of substance where Pregl used 10 mgrms. The combustion tube is of glass, 12 mm. in bore and 40 cm. long. About 4 cm. from one end the tube is tapered to 3 mm. to accommodate the small rubber-tubing which connects to the absorption tubes. The combustion tube is filled in the order named with (1) fine glass wool at the tapered end; (2) a 2·5 cm. layer of oxidised copper-wire and asbestos which has been treated with a concentrated solution of copper nitrate, dried, and ignited; (3) a 0·5 cm. layer of asbestos; (4) a 1·5 cm. layer of platinised asbestos; (5) a 0·5 cm. layer of asbestos; (6) another 3·5 cm. layer of copper oxide asbestos; (7) a 0·5 cm. layer of asbestos; (8) a 1·5 cm. layer of platinised asbestos; and, finally, (9) a 0·5 cm. layer of asbestos. The filled portion of the tube is wrapped round with one thickness of $\frac{1}{64}$ inch asbestos paper, which is secured with asbestos thread, and the tube is supported in an iron trough lined with asbestos paper, except at the end where the tube has a wrapping of this material. Alundum half-

tubes are used as tiles. Light glass tubes, weighing little more than 10 grms. when packed, are used as absorption tubes. Calcium chloride is used to absorb water, and soda lime to absorb carbon dioxide.

Detailed directions are given in the paper for reducing to a minimum certain errors which, though small absolutely, tend to represent notable percentages where the total quantities handled are so small. A combustion, with all its attendant weighings, can be completed within two hours, and the accuracy of the results for carbon appear to be limited only by the sensitiveness of the balance employed. The hydrogen results are somewhat less satisfactory, and the author considers that they would be only slightly improved even if a micro-balance were available. Nevertheless, the method has proved very useful, especially in biochemical work, where very small quantities of material are sometimes available. G. C. J.

GOVERNMENT REPORT.

Report of the Fuel Research Board. Pp. 10. Price 2d. (London: H.M. Stationery Office, 1917.)—This Report, signed by Sir George Beilby (Director) for himself and the Hon. Sir Chas. Parsons, Sir Richard Redmayne, and Sir Richard Threlfall, is a model in many respects, and not least in its brevity, at a time when, in spite of the Paper Controller, every post brings some of us reams of paper wasted by Government departments. The Board announce that the South Metropolitan Gas Company have leased to the Government at a peppercorn rent four acres of land at the East Greenwich Gas Works for the erection of a Research Station, and have agreed to take over at market prices the surplus products, gas, tar, liquor, and coke, resulting from the operations at the station. The site is a strip of level ground, situated on the main siding which connects the gas works with the South-Eastern Railway, and with access to an existing road. On this site it is proposed to erect (1) an Unloading Platform, provided with sampling floor, a coal-breaker and screens, a weighing machine, an elevator, and high-level bunkers; (2) a Retort House, designed as an experimental house—that is to say, with provision for carrying out quickly necessary changes in the apparatus installed in it; (3) a Condenser and Exhauster House; (4) Gas Holders; (5) a Gas Producer House; (6) a Steam Boiler House; (7) a Briquetting House; (8) Tar and Oil Stills and Condensers; (9) a Gas Furnace House for testing gas furnaces, annealing ovens, and the like; and (9) Laboratories, Workshops, and Offices. The buildings at present contemplated should only occupy one of the four acres. Further, a large part of the equipment of these buildings will be of a permanent character, and will serve all the general purposes of a Research Station. Future extensions will, therefore, not repeat this permanent equipment, but will be based on it.

In their first Report (not published) the Board stated that they had in view two main lines of research: first, a survey and classification of the coal seams in the various mining districts by means of chemical and physical tests in the laboratory; and, second, an investigation of the practical problems which must be solved if any large proportion of the raw coal at present burned in its natural state is to be replaced by the various forms of fuel obtainable from coal by carbonisation and gasification processes. The second line of inquiry has been led up to by the general demand for

motor spirit, the Navy's demand for home supplies of fuel oil, and what may be called the municipal or corporate demand for the use of smokeless fuel, for the individual demand for smokeless fuel is as yet small. The smokeless fuel available being what it is, it is the other fellow we all wish to see compelled to use it. Clearly, low temperature carbonisation is one of the problems the new Research Station must attack.

Unlike low temperature carbonisation, which has been practised by few and with only partial disclosure of their results, the gas industry is a highly developed one, concerning which there are abundant, trustworthy data. Yet the Board, with a great national Research Station in sight, set it the question, "Can supplies of town gas be obtained more economically and conveniently by methods of carbonisation and gasification other than those at present in use in gas works ?"

Other questions are suggested by the Board. Can electric power be obtained more cheaply if the coal used for steam-raising is first subjected to processes of carbonisation and gasification ? Can the use of gaseous fuel be forwarded by the development of more scientific methods of combustion in furnaces, muffles and ovens used in metallurgical, ceramic, and chemical operations ? The Research Station should also provide data which would either encourage the attempt to utilise the peat deposits of the Kingdom or discourage further waste of energy in that direction.

The Board have produced a promising scheme; they aim at solving certain fundamental problems of great importance; they do not expect quick results; they have taken steps to reduce to a minimum delay in the conduct of experiments—for example, in the design of their retort house—and they deserve our thanks and give expectation of great results. G. C. J.

REVIEW.

THE CHEMISTS' YEAR-BOOK, 1917. Edited by F. W. ATACK, assisted by L. WHINYATES. London: Sherratt and Hughes, 1917. Pp. 1030. Price 10s. 6d. net.

The first edition of this useful little work was the subject of a review in our pages (ANALYST, 1915, **40**, 427), and the third edition, which is now before us, clearly shows that the writers have not rested from their labours, in that they have introduced a number of corrections and additions to a work which was in the first instance a model of careful correction.

We are told in the preface that "the revision on the sections on technical analysis is now entirely in the hands of experts, as it is felt that this is essential for confidence to be maintained in the reliability and up-to-date character of the sections." These experts have done much to fill their respective sections with up-to-date information, and the result leaves a happy feeling of independence of the German productions which this Year-Book so well replaces.

To expect a work with so wide a scope and with such a vast variety of information and tables to be "the last word" in every direction would be unreasonable in the extreme. An expert will doubtless find many weaknesses and omissions in his own particular branch, but to the general user these do not militate against the value of the book.

It would serve the interests of the British chemist better to point out any faults to the editor than to allow them to become mountains which would hide all the good that the work contains.

E. RICHARDS BOLTON.