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THE ANALYST.

OBITUARY.

JAMES NIMMO, F.I.C.

JAMES NIMMO, whose death at the age of sixty-four occurred on December 3, was born at Busby, near Glasgow, and received his early chemical training in the laboratory of Messrs. Wallace, Tatlock, and Clark. He was associated for a time with the late Dr. Dixon in an investigation of the chemical impurities in the air of Glasgow, and was for some time chemist in a Scottish alkali works. From there he came to London, and entered the laboratory of Dr. Bernard Dyer, with whom he remained until the time of his death. He joined the Society of Public Analysts in 1879, and was elected a Fellow of the Institute of Chemistry in 1880. He was associated with Dr. Dyer in various appointments under the Fertilisers and Feeding Stuffs Act, and was Public Analyst for Weymouth and Melcombe Regis. He rendered considerable service to the Society of Public Analysts during its earlier years by undertaking much of the clerical work associated with both the treasurership and the secretaryship; and he served on the Council of the Society in 1899-1900 and again in 1909-10.

He was very popular among his colleagues, and, until the last few years during which failing health made attendance impossible, he rarely missed a meeting of the Society during his long membership.

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

AN ordinary meeting of the Society was held on Wednesday, December 4, in the Chemical Society's Rooms, Burlington House. The President, Dr. S. Rideal, F.I.C., occupied the chair.

The minutes of the previous meeting were read and confirmed.

Certificates of proposal for election to membership in favour of Messrs. R. H. Picard, D.Sc., Ph.D., F.R.S., F.I.C.; L. G. Radcliffe, M.Sc., F.I.C.; J. Smith; F. E. Weston, B.Sc.; J. C. N. Eastick, A.I.C.; and S. H. Blichfeldt, were read for the second time; and a certificate in favour of Mr. Cecil William Wood, Analytical Chemist in the Research Department, Woolwich, was read for the first time.

The following papers were read: "Recorder for Estimating Carbon Monoxide in Inflammable Gases," by Eric K. Rideal, M.A., Ph.D., M.B.E., and H. S. Taylor, D.Sc.; "The Estimation of Phenacetin and other *p*-aminophenol Derivatives by Hypochlorous Acid," by A. D. Powell; "Effect of Morphine Concentration on the B. P. Method of Morphine Estimation," by Harold E. Annett, B.Sc., F.I.C., and Hardayal Singh, B.Sc.

THE ESTIMATION OF CACAO SHELL.

By ARTHUR W. KNAPP, B.Sc., F.I.C., and BASIL G. McLELLAN, F.I.C.

(*Read at the Meeting, November* 6, 1918.)

The estimation of cacao shell has received the attention of many able chemists, but it is doubtful if all the factors influencing the different methods or the limitations of their accuracy have been taken into account. In view of the exceptional facilities at our disposal for the examination of authentic samples, we think that some record of our joint experience may be of use.

Variation in Quantity and Character of Shell on Beans.

(*a*) *Variation due to Botanic Variety.*—The different botanic varieties have distinctly different properties, and this is one of the causes of the varying characters of the shell from cacao of different geographical origin. In many places the different varieties may be found growing on the same plantation. Thus, taking beans from cacao-trees growing side by side in Trinidad, and preparing the cacao in exactly the same way (without claying), we obtained 13·3 per cent. of shell in Trinidad criollo, and 15·1 per cent. of shell on the Trinidad calabacillo (a more hardy variety with a smaller bean).

(*b*) *Variation due to Condition and Preparation of the Bean.*—Not only does the original cacao vary, but the character of the shell varies with the ripeness of the cacao when gathered. Cacao from the same plantation, and therefore, presumably, a mixture of the same botanic varieties, was gathered in different stages of ripeness.

Raw Unclayed Trinidad Cacao.	Shell per Cent.
Unripe	14·3
Ripe	13·5
Overripe	12·3
Germinated	5·0
Unfermented	18·5
Sweepings (pascilla)	32·9

The shell on commercial cacao consists of true shell plus pulp and dirt. Every country has a different method of preparing the cacao for the market, and this affects

the character of the shell. Thus, in those countries where the cacao is not fermented or washed to remove the fruity pulp with which the bean is surrounded, some of the pulp remains dried on the shell. Hence the high figure, 18·5 per cent. for unfermented cacao given above. More or less care is taken in separating the broken beans, and about 5 per cent. of sweepings are produced, containing 33 per cent. of shell. These sweepings sometimes get mixed with the whole beans.

Washing.—In some countries the shell is washed quite clean, the pulp being entirely removed. Thus washed, Ceylon gives only 8 per cent. of shell, and whilst the shell of normal Accra cacao amounts to 12·2 per cent., that from washed Accra averages only 9·5 per cent. This gives us some idea how much of the so-called shell is true shell, and how much is dried pulp and dirt.

Claying.—As shell is sometimes used as human food, the presence of clay is of interest. In the preparation of cacao the juicy bean has to be dried, and whilst it is drying its outside is sticky and is liable to pick up any dirt with which it comes in contact. However, some of the finest cacao—*e.g.*, certain varieties from Trinidad and Venezuela—are deliberately coated with a thin layer of clay or earth.

In our opinion, the ash of clean shell does not exceed 8 per cent. (we find that the ash of Ceylon cacao shell is only 5 per cent.); the ash of those which are practically free from earth—Arriba 6 per cent., Grenada, Jamaica, and Samoa 7 per cent., Accra 8 per cent.; the ash of those which are slightly earthed, Machala and Bahia 9 per cent.; whilst Trinidad gives 15 per cent., Columbian 17 per cent., and Carupano 24 per cent. From these figures it is evident that Trinidad cacao shell contains 7 per cent. of clay, whilst Columbian contains 9 per cent. and Carupano 16 per cent. of red earth. We think one would hesitate to recommend these last three shells for human food. The amount of clay is liable to considerable variation. Thus, analyses of ten lots of Trinidad cacao gave—

Shell	...	...	...	13·5 to 17·4 per cent.
Ash in shell	...	...	...	10·4 ,, 23·4 ,,
Clay on bean	...	...	...	0·3 ,, 2·7 ,,
Clay on shell	...	...	...	2·4 ,, 15·4 ,,

(*c*) *Variation with Country of Origin.*—We give some figures below illustrating this, but it will be recognised that cacao from one country, or even from one plantation, is liable to vary considerably, so that to give reliable average figures for any particular producing area would require many analyses. The average of six samples taken monthly in 1918 gave the following shell percentages:

Ceylon	7·9
Para	10·4
Bahia	12·1
Accra	12·2
Machala	12·5
Arriba	12·7
Grenada	14·5
Trinidad	15·8

These figures are for raw shell; they were obtained by separating the shell from the beans by hand. Roasting reduces the apparent percentage of shell by 1 to 3 per cent.

We now propose to deal critically with the various processes which have been suggested for the estimation of shell.

1. Crude Fibre.

(*a*) *Official Method of the Association of Official Agricultural Chemists, U.S.A., also called Weender's and also Henneberg's Process. (See Allen's "Commercial Organic Analysis," 1909, vol. i., p. 70.)*

Results obtained by this method:

Crude Fibre: Percentage on Fat-free Material.

	Roasted Nib.	Roasted Shell.
Lührig (*Zeitsch. Untersuch. Nahrung. Genussm.*, 1905, **14**, 263-267; see *J. Soc. Chem. Ind.*, 1905, **24**, 341)	—	11·1 to 19·8
Booth, Cribb and Richards (Analyst, 1909, **34**, 134)	4·7 to 6·2	13·2 „ 16·3
Winton, Silverman and Bailey (Connecticut Expl. Station Report, 1902)	4·7 „ 6·6	13·7 „ 20·7

Effect of Size of Particles.—The above process applied to *roasted nib* in various degrees of fineness, all of which were comparable with the size of the ordinary cocoa powder of commerce, gave the following results: Very finely ground, 5·9 to 6·5 per cent.; finely ground, 7·3 to 8·5 per cent.; slightly coarser, 9·3 to 11·6 per cent. This has an important bearing on the use of the process, and shows the necessity for obtaining the samples in the same state of division. The variation is probably due to the remarkable difficulty which is experienced in extracting the fat from coarse cacao particles, the fat protecting the particles from the action of the weak acid and alkali. On the other hand, in the case of shell, we found, to our surprise, that the size had very little influence on the fibre figure. Taking a mixed shell, we ground it to various degrees of fineness and obtained the following results:

Size of Particles of Shell (Inches).	Ether (0·720) Extract (per Cent.).	Fibre on Fat-Free (per Cent.).
Whole shell.	2·46	40·3
0·083 to 0·125	2·64	15·1
0·033 „ 0·055	2·82	14·1
0·022 „ 0·033	2·83	14·1
0·011 „ 0·022	3·41	14·0
0·006 „ 0·011	3·96	14·5
0·004 „ 0·006	4·62	14·0
Less than 0·004	6·85	14·2

(The rise in the ether extract with increasing fineness is of considerable interest, suggesting that unless the cells are actually broken the extraction is incomplete, and the butyro-refractometer figure for the extracts at 40° C. rose with fineness from 57·0 to 60·0, or the refractive index from 1·4639 to 1·4659. It is evident that the extract contained a fair percentage of resins with the cacao butter.)

The method under review is a general method for grains, seeds, etc., and as it promised to be of some value for cocoa products, a modification was adopted to meet the peculiarities of this particular material. As seven experimenters all followed this process, we give the details in full. Possibly the most important modification is the use of a filter-paper in place of linen for filtration. This probably accounts for the results being higher than those on the official process.

PER CENT. OF CRUDE FIBRE ON DRY FAT-FREE MATERIAL.

	Fat (Per Cent.).	Fry's Laboratory.	Rowntree's Laboratory.	Mean.	Cadbury's Laboratory.	Mean.	Mean of all Analyses.
Pure cocoa	25·5	(*a*) 5·89	(*b*) 5·4, 5·6 (*c*) 6·0, 6·2 (*d*) 6·8, 6·8	5·50 6·09 6·78	(*e*) 5·6, 5·7, 4·6, 4·9, 5·4, 5·6 (*f*) 5·7, 5·9, 5·9, 6·0 (*g*) 5·3, 5·6, 5·8, 5·6, 5·2, 5·6	5·29 5·87 5·60	5·86
10 per cent. shell	23·6	(*a*) 7·50	(*b*) 7·3, 7·5 (*c*) 7·7, 7·9	7·39 7·83	(*e*) 6·9, 6·9 (*f*) 7·4, 7·7, 8·0 (*g*) 6·4, 7·0, 6·9, 7·6, 7·2, 7·3, 7·2	6·90 7·70 7·09	7·44
20 per cent. shell	21·5	(*a*) 8·80	(*b*) 9·1, 9·1 (*c*) 8·8, 8·8	9·06 8·82	(*e*) 7·9, 8·3 (*g*) 8·3, 8·5, 8·0, 8·1, 8·2	8·09 8·21	8·63
50 per cent. shell	15·1	(*a*) 12·76	(*b*) 13·9, 13·8 (*c*) 14·2, 14·0	13·81 14·08	(*e*) 12·6, 12·8 (*g*) 12·5, 12·9, 12·8, 12·8, 12·8	12·68 12·78	13·14
100 per cent. shell	5·1	(*a*) 19·20	(*b*) 18·6, 18·1 (*c*) 18·2, 18·5	18·35 18·33	(*e*) 16·5, 18·3, 17·3, 17·1 (*f*) 19·0, 18·8, 19·9 (*g*) 16·6, 17·0, 16·8, 16·5, 16·5, 17·3, 18·8	17·29 19·20 17·06	18·46

Process adopted for Fibre Estimation.—Extract a quantity of the substance so as to have at least 2 grms. of dry fat-free material for the estimation of the crude fibre. The fat may be removed by any approved solvent, such as ether, petroleum ether, etc. Transfer 2 grms. of dry fat-free matter to a 500 c.c.

flask, and add 200 c.c. of sulphuric acid of strength 1·25 per cent. by weight. Connect the flask with an inverted condenser, using a rubber stopper. Bring to the boil, and maintain the boiling for thirty minutes. Filter through ordinary filter-paper, wash with boiling water until the washings are no longer acid. Rinse the substance back into the flask with not more than 200 c.c. of water (use hot water if preferred), and add 2·5 grms. of sodium hydroxide (stick, flake, or other form, provided it is pure and approximately 98 per cent. strength). Boil at once, and continue the boiling for exactly thirty minutes in the same manner as directed above for the treatment with acid. Filter at once rapidly, either (*a*) through double tared or counterpoised filter papers, wash with boiling water until the washings are neutral, dry in steam-oven to constant weight, weigh, incinerate completely, and weigh again ; or (*b*) through a single filter-paper. Wash with boiling water until the washings are neutral, and then wash the fibre into a tared dish and evaporate to constant weight. The fibre is then ignited in the dish and the ash determined. The loss in weight in either method is considered to be crude fibre.

Errors due to the Process.—We decided to determine how far analysts following the prescribed process would agree. Hand-picked, shell-free cocoa and cocoa-free shell were prepared on a large scale, and these were mixed in certain proportions, and examined by seven analysts who were unaware of their composition. The results are expressed to only one place of decimal, but the averages are calculated on the actual figures obtained. In these tests we had the advantage of the co-operation of Dr. Bywaters (of Messrs. Fry and Sons).

An examination of these figures shows the fibre estimation—(1) does not give such good duplicates as might be expected; (2) is greatly influenced by the personal equation. If an analyst only makes one estimation, he may get an experimental error of 6 to 8 per cent. on the shell percentage. However, we will assume that he takes the mean of at least two estimations, and that he accepts 5·8 as the fibre figure for cocoa and 18·5 as the fibre figure for shell, then from the above table we obtain the following results :

PER CENT. OF SHELL IN COCOA.

Present.	Found by Analysts—						Mean.
	(*a*)	(*b*)	(*c*)	(*e*)	(*f*)	(*g*)	
10	10·2	9·6	12·2	6·6	11·4	7·8	9·9
20	18·5	20·1	18·7	14·2	—	14·9	17·5
50	46·5	53·6	55·4	46·0	—	46·7	49·1

Several analysts found small quantities up to 5·7 per cent. of shell in the pure cocoa, and, as will be seen from the table, found from 6·6 to 12·2 per cent. in a cocoa containing 10 per cent. It would appear that even when the process is carefully defined it is necessary for each analyst to determine his own figures for pure cocoa and pure shell from the average of a large number of results.

We have made a few experiments with a view to increasing the agreement between different analysts.

(1) *Filtering.*—We prefer filter-paper to linen, because of the extreme fineness of the cocoa particles, and also because of the difficulty of defining the exact mesh for linen. We have used 12·5 cm. Swedish and Whatman No. 1, and find they give very similar results. The objection to filter-paper is the difficulty of removing the material without bringing away some of the filter-paper itself. It may be that copper gauze with 100 meshes to the linear inch (Fairley and Burrell, *J. Soc. Chem. Ind.*, 1918, **37**, 155T), or an even closer mesh, would prove the most satisfactory filtering medium.

(2) *Strength of Acid and Alkali.*—We find that within narrow limits the variation in the strength of sulphuric acid and sodium hydroxide used is of little importance.

(3) *The Time of Boiling.*—The time of boiling should be rigidly adhered to, especially in the case of the alkaline treatment. The rate of boiling might with advantage be standardised, possibly by the use of an oil-bath at 120° C.

(4) It will be found more convenient to wash off the acid residue with 175 c.c. of hot water, and add 25 c.c. of 10 per cent. sodium hydroxide, instead of using 2·5 grms. of the solid, as given in the above process.

Differences due to Variation in the Nature of the Shell.—The percentage of fibre in the shell is naturally affected by the ripeness of the cacao when gathered and the amount of fermentation it undergoes. Cacao from the same plantation in Trinidad was carefully collected in bulk in an unripe, ripe, over-ripe, and germinated condition, and fermented separately. Some ripe cacao was dried without fermentation. The mean of two estimations for fibre gave the following figures:

	Per Cent.
Unripe	14·3
Ripe	17·0
Over-ripe	16·0
Germinated	21·2
Unfermented	19·0

These figures help one to understand the variations which occur with beans from different countries.

Country of Origin.—The various beans were given a low-temperature roast (the interior of bean probably not exceeding 120° C. to 130° C.). The shell was picked off by hand (the germs being excluded), ground, and passed through a sieve (diameter of holes 0·02 inch). It was then extracted for twenty-four hours, and dried in a water-oven. Two analysts, (*a*) and (*b*), determined the fibre by the method described, and each analyst did at least two estimations on each sample. The results are only expressed to one decimal place, as to give more would be indicating that the process is capable of greater accuracy than it is.

The number of factors influencing the percentage of fibre is so great that an examination of the above table reveals no obvious relation between the fibre and the botanic variety of the bean, its fermented condition or other natural property. If we assume as before, for calculation purposes, that shell contains 18·5 per cent. of fibre, then, if we have 20 per cent. of shell in the fat-free material, we shall find

15·4 per cent. or 24·0 per cent. of shell according as the shell is that of Grenada or Accra beans. It should not be forgotten, however, that as a rule commercial cocoa is a blend of two or more different kinds of bean. Our figures are in general agreement with those of Winton, Silverman, and Bailey, who obtained a minimum of 13·7, a maximum of 20·7, and a mean of 18·0.

FIBRE IN ROASTED CACAO SHELL.

Cacao Shell.	Fibre on Fat-Free.		Mean.
	(*a*)	(*b*)	
Arriba (low roast)	14·9	15·9	15·4
Grenada	15·3	15·5	15·4
Machala	16·5	16·9	16·7
Arriba (high roast)	17·8	18·6	18·2
Trinidad	20·4	17·0	18·7
Ceylon	19·0	20·4	19·7
Accra (well fermented)	20·0	20·8	20·4
Bahia	20·8	20·2	20·5
Para	20·4	21·0	20·7
Accra (common)	21·3	21·6	21·4
Average	18·64	18·79	18·7

Effect of Roasting.—It is unlikely that the analyst will encounter raw shell in cocoa; however, a small amount of raw shell is separated in cleaning the beans, and this raw shell might conceivably be used in cocoa, but the shell on the market is always more or less roasted. The surmise that roasting would increase the percentage of fibre was found to be correct. The figures given are the mean of two or three analyses on the same sample. With Ceylon (criollo) cacao shell we obtain raw 17·5 and roasted 20·4. (Winton, Silverman, and Bailey, working on Caracas beans, found in the shell: fibre per cent. raw, 14·7; under-roasted, 15·4; medium roasted, 16·5; over-roasted, 16·6.) With West African (forastero) cacao shell, we obtained raw 18·2, and roasted 20·6. With Arriba cacao shell, low roast 15·4, and high roast 18·2. As the cacao bean is subjected to varying degrees of roasting according to the kind of cocoa or chocolate required, all the analytical figures for shell are liable to variation from this cause.

(*b*) *König's Method* (ANALYST, 1898, **23**, 47; and Zipperer, *Die Chocolade-Fabrikation*, 280, German Edition, 1913).

In this method 3 grms. of the defatted substance are treated with 200 c.c. of glycerol (1·23 sp. gr.), containing 20 grms. per litre of concentrated sulphuric acid, under the pressure of 3 atmospheres for one hour. It is then filtrated whilst hot through an asbestos filter, and after being washed successively with hot water, alcohol, and ether, it is weighed, then burnt, and the ash weighed. The difference between the two weighings expresses the amount of ash-free crude fibre.

Criticisms on the Method.—The method has met with considerable adverse criticism (Gury, ANALYST, 1912, **37**, 447), and has been modified by Filsinger (*Zeitsch. Analyt. Chem.* 1900, 223) and by Matthes and Müller (*Zeitsch. Untersuch. Nahrungs. Genussm.* 1906, **15**, 159; also ANALYST, 1906, **31**, 159); but as the figures obtained varied from 5·5 to 9·7 per cent. for nib and from 13·1 to 1 8·2 for shell, the process has nothing to recommend it as compared with the simpler method previously described.

2. NITROGEN.

The Kjeldahl-Gunning process was used for the determination of nitrogen, and the utmost care exercised in obtaining pure nib-free shell and pure shell-free nib, the samples being hand-picked. The shell contained no germs. The nitrogen was determined on two separate samples of shell drawn on different days. In the first sample the nitrogen was determined direct on the shell, in the second sample on the fat-free material. As we were unable to obtain petroleum ether, trichlorethylene was used for extraction; this solvent dissolves out some of the theobromine.

NITROGEN IN ROASTED SHELL.

Cacao Shell.	Fat (per Cent.).	Nitrogen (per Cent.).		
		Estimated en Original Shell.	Calculated on Fat-Free.	Estimated on Fat-Free.
		(*a*)	(*a*)	(*b*)
Ceylon	2·00	1·76	1·80	1·95
Para	2·30	1·99	2·05	1·98
Arriba	4·24	2·08	2·17	2·11
Machala	6·55	2·43	2·60	2·51
Grenada	2·36	2·75	2·81	2·69
Accra (common) ...	2·45	2·76	2·83	2·67
Accra (well fermented) ...	4·57	2·86	3·00	3·01
Trinidad	2·64	2·96	3·04	3·01
Bahia	2·02	3·18	3·25	3·23
Average	3·23	2·53	2·61	2·57

We found that samples taken from different bags of the same consignment often gave good duplicates, and two lots of British West African cacao purchased in Accra and in Liverpool both gave 2·86 per cent. of nitrogen.

We do not suggest that the figures in the table can be taken as giving the average percentage of nitrogen in the shell on beans from a particular country. To give figures which could be so applied many analyses would have to be made. The figures do, however, give some idea of the range of nitrogen figures for shell. The table below serves the same purpose for nib. The nib came out of the shell in which the nitrogen was determined above (columns marked *a*).

NITROGEN IN ROASTED NIB.

Cacao Nib.	Fat (per Cent.)	Moisture (per Cent.).	Nitrogen (per Cent.).	
			In Original Nib.	Calculated on Dry Fat-Free.
Trinidad	53·94	2·49	2·07	4·75
Bahia	56·14	2·32	2·08	5·01
Para	55·03	2·77	2·19	5·19
Accra (common) ..	55·47	1·74	2·22	5·19
Ceylon	52·08	1·54	2·38	5·13
Accra (well fermented)	52·76	2·61	2·36	5·29
Machala	52·38	2·19	2·39	5·26
Grenada	53·96	2·07	2·38	5·41
Arriba	51·73	2·25	2·72	5·91
Average	53·72	2·22	2·31	5·23

Effect of Roasting.—This is of interest because of the very different amount of roasting which beans undergo for different purposes.

NITROGEN (PER CENT.)

	On Original.		Calculated on Dry Fat-Free Nib.	
	Raw.	Roasted.	Raw.	Roasted.
Bahia nib	1·98	2·08	4·75	5·01
Accra (well-fermented nib) ...	2·04	2·36	4·90	5·29
Ceylon nib	2·27	2·38	5·31	5·13
Bahia shell	2·81	3·18	—	3·25
Accra (well-fermented shell)	2·66	2·86	—	3·00
Ceylon shell	1·69	1·76	—	1·80

The variation due to roasting is appreciable. Winton, Silverman and Bailey found only slight changes, but other experimenters (Zipperer and Ridenour) have found even greater differences. It is reasonable to suppose that in those cases where the cacao is moistened with alkaline carbonates before roasting some nitrogen would be lost.

Criticism.—The value of this figure for the estimation of shell in cocoa is small However, it has the advantage of being a figure which can be very accurately determined. The variation in the percentage present in fat-free nib is appreciable (we find from 4·75 to 5·91; Winton, Silverman, and Bailey found 4·74 to 5·41), whilst that in shell is very great (we find from 1·80 to 3·25; Winton, Silverman, and Bailey found 1·87 to 3·41). This great variation is not remarkable when we consider

that we have so great a variety of shell, and that we have theobromine and caffeine as well as a complex mixture of proteins present. In a general way those beans which give a low nitrogen figure for the nib have a high percentage of nitrogen in the shell. In any calculation the germs appear as cocoa, since the dry fat-free germ contains about 6 per cent. of nitrogen. The danger of relying on the percentage of nitrogen to estimate shell may be shown by taking an extreme case. Suppose we imagine Bahia shell mixed with fat-free Arriba nib, then we could have 25 per cent. of shell present before the figure came below the average for nib, or 43 per cent. of shell before the figure came below that for Trinidad nib. This is only by way of illustration. as in practice one has to deal, not with one kind of bean, but with a blend.

3. Elutriation and Flotation Methods.

(*a*) *Filsinger and Drawe's Process* (*Zeitsch. öft. chem.*, 1899, **5**, 27, *ibid.*, 1903, **9**, 161; Analyst, 1903, **28**, 216).

Two grms. of the finely powdered fat-free substance are placed in a porcelain dish with 100 c.c. water, and boiled (with continuous agitation) until the powder is thoroughly moistened and the froth disappears. The dish is allowed to stand for five minutes, after which the upper part of the liquid is poured off. It is again filled up with cold water which is allowed to stand, and then poured off. This process is continued until the supernatant liquor is quite clear. The liquid is then given a circular motion and allowed to stand until the solid material is completely settled, after which the liquid is drained off. This is repeated until the supernatant liquor no longer contains any floating particles. The sediment is washed into a Gooch crucible, dried and weighed. The weight obtained is multiplied by the factor 1·43, obtained by Drawe, and corrects for soluble matter in the shell. The figure so obtained directly represents the quantity of shell present.

Criticisms of the Method.—Ulrich (*Arch. Pharm.*, 1911, **249**, 537) obtained for roasted nib 0·63 to 0·73, and for roasted shell 57·85 to 85·17. As a result of his figures he suggests that the factor of 1·43 obtained by Drawe should be increased to 1·72. The fact that one observer has to use a factor of 1·43, while another recommends 1·72, shows that the method is only comparative and subject to personal error.

There can be no doubt that the results obtained with this method are largely dependent upon the sizes of the particles of shell and nib, and also on the manufacturing treatment which the cocoa has received.

(*b*) *Macara's Process* (*Bolton and Revis*, "*Fatty Foods*," p. 304; *and Baker and Hulton*, Analyst, 1918, **43**, 199).

An outline of the process is given, from which we have worked out the following more detailed procedure:

Fat is completely removed by extraction with petrol from some 10 to 20 grms. of the cocoa, the extraction being continued until the petrol ceases to show even traces of fat when evaporated on a watch-glass. Five grms. of the fat-free material are weighed out and ground up with water in a mortar. The mortar is then filled with water, and after allowing a minute or two to settle, the cocoa, still in suspension,

is poured into a cylinder. (The dimensions of the cylinders used were 41 to 43 mm. diameter by 280 mm. in height.) The residue still in the mortar is ground up with a further quantity of water, and poured off in the same way into the cylinder until all the material has thus been washed into the cylinder. The cylinder is then filled up with water, thoroughly shaken, and allowed to stand for fifteen minutes. The liquid is syphoned off to within a short distance of the residue lying on the bottom. Ten such elutriations take place, and the liquid is allowed to stand after each for the following times: 15 minutes; 15 minutes; 10 minutes; 7 minutes; and then 6 periods of 5 minutes each. By this time practically no matter should remain in suspension. The residues are then washed on to tared filter papers, dried and weighed, and the ash of the residues deducted from the weights so obtained. It has been found that it is quite convenient to do six samples at a time, and that the time occupied in filling up and shaking the cylinders is practically equal to the time occupied in siphoning off the liquor. By this process we obtained the following results, showing variation with kinds of cacao:

RESIDUE OBTAINED FROM 100 GRMS. OF FAT-FREE.

Cacao.	Roasted Nib.	Roasted Shell.
Bahia	0·28	19·4
Trinidad	0·40	20·4
Grenada	0·90	23·9
Java	1·40	24·7
Ocumare	0·40	26·9
Accra	0·40	29·6
Arriba	0·10	30·7
Mean	0·28	25·2

Criticisms of the Method.—This process, being a modification of the Filsinger-Drawe process, is subject to the same criticisms. With cocoas which were known to contain a large percentage of shell and which had been submitted to the "Dutch" process, we have obtained figures for sediment which would classify these as free from shell.

For the experiments below the details of the process more closely resembled those described by Bolton and Revis, in that 10 grms. of defatted material were taken, the periods of standing were 15, 15, 10, 5, 5, 5, 5, and 5 minutes, and the residue was dried and weighed in a tared platinum dish. Revis and Bolton recommend 10 grms. to be defatted and the shell to be estimated on this 10 grms.. in which case the Soxhlet thimble would have to be scraped clean. It is obviously better to run a fat estimation at the same time, and take an accurately weighed portion of the fat-free substance. The fat-free residue is ground in a mortar. It is practically impossible to standardise this grinding, which, unfortunately, considerably affects the result. Thus a fat-free cacao mass when ground for five minutes gave 38·7 per cent. residue,

and when ground for 10 minutes 26·8 residue. We decided to grind the material for fifteen minutes.

In Revis and Bolton's account they state that with shell 90 per cent. of the residue can be distinguished as spiral vessels and sclerenchymatous tissue. In practice we find the pure shell powder does not give more than 40 per cent. of such material, the remainder being masses of cells of indefinite structure.

In some experiments performed under our direction by Mr. J. H. Hicklin, M.A., the greatest care was taken to extract the very last trace of fat, the conditions for adding the water to the cylinder were standardised (it was found an advantage to hold the cylinder slightly at an angle, so that the water ran smoothly down and did not form bubbles), and the procedure in siphoning was carefully considered. The siphon was turned up one-tenth the height of the water (*i.e.*, depth occupied by 50 c.c.); it was always lowered gradually, and was lowered until the bend just touched the upper surface of the sediment. The times of "resting" were most rigidly adhered to. In spite, however, of the most elaborate precautions, duplicates did not agree well, and the results for 5, 10, 15, 20, 25, 30, 50, and 100 per cent. shell when plotted did not lie on a straight line.

Shell per cent.	0	5	10	15	20	25	50	100
Residue per cent. ...	2·2	3·5	2·4	3·5	3·8	3·2	7·1	29·2

It should be noted that the above experiments were performed on shell which we ourselves ground very fine, but which was not sieved.

Macara (*loc. cit.*) mentions that the percentage of husk varies according to the *degree of fineness* to which the cocoa has been ground. The figures below show that the effect is so great as to render the process useless. A cacao shell powder was separated into parts of various sizes.

Size of Shell.	Residue.	Calculated Shell.
0·004 to 0·009 inch	34·0 per cent.	100 per cent.
0·003 „ 0·004 „	12·5 „	34 „
Less than 0·009 inch	0·6 „	0 „

As 80 per cent. of the ground shell was less than 0·003 inch in diameter, the significance of its giving a figure lower than that of cocoa is evident.

Thinking possibly that we were not working the process in a satisfactory manner, we sent samples containing this shell to a well-known analyst who had faith in the process. In a cocoa containing 13·5 per cent. of shell he found 3 per cent. by the Macara process, and in a cocoa containing 27 per cent. of shell he found 0 per cent., although by other methods he was convinced that shell was present.

(*c*) *Flotation Method—Goske's Process of Flotation in Calcium Chloride Solution* (ANALYST, 1910, **33**, 162).

One grm. of the dry fat-free cocoa is mixed with a stoppered tube with 20 c.c. of a calcium chloride solution prepared by dissolving 107·1 grms. of calcium chloride in

100 c.c. of water (this solution should have a sp. gr. of 1·535 at 30°C.). The stopper of the tube is then removed, the mixture is heated to boiling for two minutes, and while still hot submitted to centrifugal action for six minutes. The liquid portion is now removed, and the almost solid sediment is collected on a weighed filter, washed with hot water until free from chloride, dried at a 100°C., and weighed. From the weight of the sediment of husk obtained the excess quantity of the latter present in the original cocoa is calculated. For this purpose it may be taken that cacao husk itself yields 38·7 per cent. of sediment, and the amount of fat in the cocoa must also be taken into consideration. The figure 38·7 was the highest result obtained on the examination of a number of samples of cacao husk, the average result being 24·5 per cent. From the final result obtained a deduction of 6 per cent. is made, this being the quantity of husk yielded by ordinary commercial cocoas.

Criticisms of the Method.—We find the process has many difficulties in practice. It is to be regretted that Goske did not find some suitable solution of sufficient density other than calcium chloride. A solution which sets to a solid mass the moment it is allowed to cool is inconvenient in use. It renders difficult what is essential to success, the obtaining of a homogeneous mixture of cocoa and solution, and further it tends to set during the centrifugal action. In the presence of these difficulties we have failed to obtain satisfactory results with this method on pure cocoa and shell, and the figures on mixtures suggest that either the cocoa floats the shell up, or the shell drags the cocoa down. Filsinger and Bötticher (*J. Soc. Chem. Ind.*, 1910, **29**, 1129), and Duboïs and Lott (*J. Ind. Eng. Chem.*, 1911, **2**, 251), and Schenk, Schmidt, Görbing (*Zeitsch. öft. Chem.*, 1912, **18**, 201), have failed to get satisfactory results by this method, which, in our opinion, is unreliable.

Process suggested by Kulusky (*Zeitsch. Untersuch. Nahrungs. Genussm.*, 1912, **21**, 654).—This process also depends on the difference in specific gravity of the shell particles and nib particles, and is open to the same criticism as the Goske process. So also is the process suggested by H. Grosse. (*See J. Soc. Chem. Ind.*, 1916, **35**, 137).

4. Pentosan.

(*Tollens and Kröber's Process. J. f. Landw.*, 1900, 357; *and Hehner and Skertchly*, Analyst, 1899, **24**, 178-183.)

From the quantity of weighed black precipitate of furfurol-phloroglucinol, the quantity of furfurol can be calculated by division by 1·84, or, more correctly, by means of the figures given in Tollens' table (König, Unters. Landw. u. Gewerbl. wicht Stoffe, 225). From the quantity of furfurol we can obtain the amount of pentosan as follows: Furfurol—0·0104 grm. × 1·88 = pentosan.

Several other methods have been suggested for calculating this figure, and are as follows:

Calculation Formulæ.—Let a = weight of furfurol-phloroglucide, p = weight of pentosan required.

(*a*) *Dekker.*—$p = \left[\left(\frac{a}{1} \times \frac{1}{1{\cdot}84}\right) - 0{\cdot}0104 \text{ grm.}\right] \times 1{\cdot}88.$

(*b*) *Tollens* (*J. Soc. Chem. Ind.*, 1907, **26**, 987).—$p = (a + 0{\cdot}0052) \times 0{\cdot}8824$.

(*c*) *Kröber* (Allen, "Commercial Organic Analysis," vol. i., p. 403).—(For weights of precipitate from 0·03 to 0·3 grm.) $p = (a + 0{\cdot}0052) \times 0{\cdot}8866$.

(*d*) From weight of phloroglucide obtain pentosan from Wiley tables per cent.

(*e*) *Formula Adopted.*—$p = (a + 0{\cdot}0052) \times 0{\cdot}89$.

Results obtained by this method:

PENTOSAN: PERCENTAGE ON THE FAT-FREE MATERIAL.

	Roasted Nib.	Raw Nib.	Roasted Shell.	Raw Shell.
Warnier (*Zeitsch. Untersuch. Nahrungs. Genussm.*, 1899, **8**, 892) ...	—	5·0	—	—
Hehner and Skertchley (ANALYST, 1899, **24**, 178-183)	—	2·7	—	8·9
Lührig and Segin (*Zeitsch. Untersuch. Nahrungs. Genussm.*, 1906, **15**, 162)	—	2·5 to 4·6	—	7·6 to 11·2
Brochnow ("Dissertation Braunschweig," 1908)	3·9 to 4·6	3·8 ,, 4·8	7·9 to 9·9	—
R. Adan (Seventh Internat. Congress App. Chem., 1909, Section VIIIc., 194)	2·3 ,, 3·6	2·7 ,, 3·8	—	7·6 ,, 10·5
Dekker (Ulrich, *Arch. Pharm.*, 1911, **249**, 549)	—	4·3 ,, 4·8	9·0 to 9·6	8·2 to 9·6
Welman (*Zeitsch. öft. Chem.*, 1911, **17**, 500)	—	—	—	7·5 ,, 8·5
Ulrich (*Arch. Pharm.*, 1911, **249**, 551)	3·9 to 4·3	3·9 to 4·3	8·2 to 9·7	8·2 ,, 9·8

Criticisms of the Method.—The paper by Adan (*loc. cit.*) created much interest in this process, but it has not stood the test of time. The process is tedious, and requires great manipulative skill to obtain satisfactory duplicates, and there is no general agreement as to the correct formula to calculate the pentosan present. The chief objection is the wide range of values; thus, we obtained from 3·3 to 5·2 for various roasted nibs, and 7·7 to 10·0 for roasted shell. It will be noted that the highest figure for nib approaches the lowest figure for shell.

One of us found difficulty in getting good duplicates with phloroglucinol, and so we tried the use of Fehling solution to estimate the furfurol, following the process recommended by Eynon and Lane (ANALYST, 1912, **37**, 41-44), and using Kröber's table to calculate the pentosans. The results were little better, the disagreement apparently being due to the different amounts of reducing bodies produced. Further, we found that the mere addition of boiling water to aid in grinding the shell, with subsequent evaporation of the water, greatly reduced the percentage of pentosans obtained, one shell giving as low a figure as 4·7.

Jolles (*Zeitsch. Analyt. Chem.*, 1906, 196) prefers to titrate the furfurol, using bisulphite.

Jäger and Unger (*Ber.*, 1902, **35**, 4440) state that other substances distil over which upset the subsequent precipitation and cause a precipitate which is not the same as when pure furfurol is used. It is only rarely that all the furfurol is distilled over at 400 c.c., 500 to 600 c.c. usually being necessary. They state that a much more uniform precipitation is affected by the use of barbituric acid. (Precipitate × 0·4659 = furfurol.)

Results obtained by Barbituric Acid Method:

PENTOSAN: PERCENTAGE ON THE FAT-FREE MATERIAL.

	Raw Nib.	Raw Shell.
Devin and Strunk (Ulrich, *Arch. Pharm.*, 1911, **249**, 549)	1·0 to 1·6	3·0 to 5·3
Prochnow ("Dissertation Braunschweig," 1908) ...	—	6·3 „ 8·6

Criticisms of the Method.—The refinement suggested by Jäger and Unger does not improve matters appreciably, the figures which we obtained for roasted nib being 2·6 to 4·3, and 8·8 to 9·0 for roasted shell, natural variations which are great enough to render the process of little or no value. Prochnow concludes from his results, noting the great variations between them and those of Dekker and Lührig and Segin, that the pentosan determination is of no great value for the determination of shell in cocoa. Ulrich states that his results and those of other investigators prove that this method for determination of shell in cocoa has no value when the shell content is below 30 per cent.

5. "COCOA RED" METHOD.

Ulrich (ANALYST, 1912, **37**, 52) obtained the following percentages of ferric chloride precipitate on the fat-free material: Roasted nib, 10·7 to 16·8; raw nib, 12·1 to 17·1; and shell, 0. Our figures show a wider range for nib, and from 1·3 to 4·8 for shell.

FERRIC CHLORIDE PRECIPITATE PER CENT. ON FAT-FREE MATERIAL.

Cacao.	Roasted Nib.	Roasted Shell.
Arriba	22·1	1·3
Accra	22·0	3·1
„ unfermented (1)	14·0	—
„ „ (2)	12·7	—
Bahia	21·2	—
Trinidad (1)	20·0	—
„ (2)	9·6	—
„ unfermented	12·2	—
Grenada	17·0	—
Ocumare	15·7	1·3
Java	15·6	—
Mixed shell, pure commercial samples (1) ...	—	2·2
„ „ „ (2) ...	—	3·6
„ „ „ (3) ...	—	4·8

Ulrich only claims for his method that "the presence of 10 per cent. and upwards of shell can generally be ascertained." This modest conclusion is arrived at by the consideration of a mass of figures expressed to four places of decimals. Ulrich is apparently of opinion that only "cocoa red" is estimated. Actually other tannin compounds are precipitated at the same time (note the figures on unfermented nib above). He quite incorrectly assumes that the cocoa red is entirely absent from the cacao shell. The criollo cacao bean is often almost white, and cocoa red is developed during fermentation, and consequently a highly fermented cocoa is richer in cocoa red than one which has been mildly fermented. During the fermentation tannin compounds spread from the beans to the shell. Zipperer (*loc. cit.*) gives the cacao-tannic acid, soluble in 80 per cent. alcohol, in raw shell as varying from 3·80 to 9·15 per cent. Taking these facts into account, we cannot recommend Ulrich's lengthy process; possibly, when we have a more definite knowledge of the tannin compounds present in cacao, a useful method may be devised for the estimation of cocoa in shell powder, but the variation in the figure for nib will always be fatal to its use for the estimation of small quantities of shell in cocoa.

6. Methods involving Use of the Microscope.

Before the grinding of cocoa essence became such a fine art, it was possible, by means of the microscope, to identify with certainty the larger particles of shell, and to form an approximate idea as to the quantity of shell present. With the advent of modern machinery, more thorough grinding of the cocoa is effected, and the distinction between particles of shell and particles of nib becomes more difficult. Processes have been suggested in which use is made of stains for colouring the particles of shell or nib.

"*Ruthenium Red*" *Method.*—We find the following the best method of using this:

Mix the sample with 5 per cent. solution of lead acetate. Add a few drops of ruthenium red dissolved in lead acetate. This stains the mucilage cells a bright pink. About 10 per cent. of an average shell powder becomes stained, but the results are rather irregular, and we find it impossible to distinguish between cocoas containing 15 per cent. and 30 per cent. of shell. This process was the subject of much discussion in the famous legal case in 1910.

H. B. Gerrans, "Detection of Cocoa Husk" (J. Chem. Tech., 1916, p. 17.)—This process depends on the theory that shell absorbs a solution of ferric chloride, whilst cocoa does not. Ferrocyanide is finally added, which stains the shell blue. We experimented with this method, and found that many particles of shell showing obvious shell structure do not stain. There is some danger of getting a precipitate of ferric ferrocyanide, which may be taken for shell. We tried removing the fat, but found that fat-free shell did not stain, and that the size of particles makes no difference. The process is valueless, as much as 30 per cent. of shell escaping detection.

The method of Wasicky and Wimmer (Analyst, 1916, **41**, 46) requires ultra-violet light and a special microscope. It suggested to us the use of the light from a

mercury lamp. By this light the cacao particles appear bluish-green and the shell greenish-brown. The opacity of the particles interferes, and the method has no quantitative value. Of the various methods we have tried, we prefer that worked out at our suggestion by Mr. Hicklin :

New Method : Phloroglucinol and Iodine Staining.—Phloroglucinol was used as a possible stain for isolating shell tissue. It was found that while this did not give a stain indicating lignified tissue—*i.e.*, "cherry-red"—yet it cleared the shell particles and heightened the colour somewhat. After treatment with phloroglucinol, iodine was added before putting on cover-slip. This stained the starch of the cacao and left the shell untouched. In this way shell particles were clearly isolated.

Details of Process.—Put about 0·25 grm. of sample in a very small beaker, and add 2 to 3 c.c. of phloroglucinol (phloroglucinol 1 grm., rectified spirit 20 c.c., distilled water 80 c.c.). Mix thoroughly, and allow to stand for fifteen minutes. Pour off the bulk of the liquid and transfer a small quantity to a slide. Add a spot of pure hydrochloric acid and a spot of $\frac{N}{10}$ iodine. Mix thoroughly with a glass rod and put on a cover-slip. In this form the preparation will soon dry and be useless for examination. Hence, if it be desirable to keep the slide more than a few hours, the mount should be treated as follows : After adding iodine and stirring, allow the slide to stand to dry, protected from dust. When dry add drop of glycerol, stir well, and place on the cover slip.

We consider this process an improvement on any of the methods we have tried, but it is liable to all the usual errors associated with microscopic methods. Apart from the fact that with finely ground cocoas it is impossible to distinguish with certainty between particles of shell and particles of nib, we have no definite proof that the colouring agents used exercise an absolutely selective action. There is also the great question of sampling and the personal variation which must occur in preparing the microscopic slides. Consequently, the microscopic processes for cocoa although they give useful information in experienced hands, cannot be regarded as giving quantitative results. A mixture of 20 cocoas gave on sieving—

0·004 inch to 0·009 inch	...	...	...	20 per cent.
0·003 inch ,, 0·004 inch	...	...	...	74 ,,
Less than 0·003 inch ...	...	...	...	6 ,,

Sieving separates and measures aggregates, not the actual particles. Under the microscope the average size of the cocoa particles was 20μ (0·0008 inch), and of the shell used in our experiments 30μ (0·0012 inch).

7. Colour of Ethereal Extract.

O. Keller (*Arch. Pharm.*, 1917, **255**, 405) founds his process on his observation that the ethereal extract of pure cacao kernels is colourless or faintly yellow, whilst the extract of husks is distinctly brown. The colours are estimated by comparison with a solution of ferric chloride containing 0·1 grm. iron in 100 c.c. The extract from pure powdered bean is matched by 2·4 c.c. and shell by at least 3·5 c.c., the average being 4·4 to 4·5. The author's figures show that the process is useless for *estimating* shell. We investigated the process, and found that the colour was not

seriously affected by the wetness of the ether, nor by the treatment of the shell with alkali, nor by contact with iron machinery. But the figure obtained is very appreciably affected by the fineness of the shell; the smaller the particles the greater amount of colour is extracted (for variation in amount of extract with fineness, see under Fibre Estimation). Thus, with West African cacao we obtained the following figures: Raw shell, coarse pieces, 3·0; finely ground, 12·0. Roasted shell, coarse pieces, 6·5; finely ground, 10·0. Alkalised shell, coarse pieces, 4·0; roasted shell, finely ground in iron mortar, 14·0.

8. Ash Content and Alkalinity of the Ash.

The use of these to estimate shell was proposed by Lührig (*Zeitsch. Untersuch. Nahrungs. Genussm.* 1903, **12**, 161, and Analyst, 1905, **30**, 206). For a general discussion of the ash of cacao shell, see Baker and Hulton (Analyst, 1918, **43**, 193). The wide variation in the ash content of the shell of various types of cacao, due to treatment on the plantation, has already been dealt with, and the effect of the processes at the factory on the ash content is considerable. We find this figure of practically no value for the estimation of shell, although it gives useful hints on the method of manufacture of the cocoa. In the paper by Baker and Hulton the mean analyses of pure shells were given. It will be of interest to give analyses of actual factory outputs—that is, of the shell which might be used for purposes of adulteration. Below we give analyses of the principal commercial shells, sold on the English market in bulk. These are obtained from mixtures of many varieties of cacao, and give one an accurate idea of the kind of shell actually available in quantity.

Ash of Cacao Shell (1918): Percentage Composition.

Shell.	Total Ash.	Ash Insoluble in Water.	Ash Soluble in Water.	Alkalinity of Water-Soluble Ash (as K_2O).	Chlorine (as NaCl).	Fat.	Moisture.
1.	14·42	2·89	11·63	5·69	0·22	8·8	10·5
2.	11·60	7·77	3·83	1·93	0·37	3·0	10·0
3.	10·14	5·70	4·44	1·66	0·10	4·2	8·2
4.	9·96	6·99	2·97	1·34	0·19	12·7	2·7
5.	9·69	4·67	5·02	2·55	0·33	9·0	9·1
6.	8·87	3·33	5·54	2·12	0·12	11·9	3·0
7.	8·74	4·07	4·67	2·28	0·44	5·8	3·8
8.	8·34	3·53	4·81	2·23	0·22	5·2	9·0
9.	7·83	3·02	4·81	2·34	0·34	3·6	8·7
10.	7·80	3·58	4·22	1·91	0·12	5·0	10·6
11.	7·78	3·29	4·49	1·72	0·06	9·3	3·2
12.	7·69	3·00	4·69	2·19	0·15	3·9	8·1
13.	7·32	3·07	4·25	2·02	0·29	3·0	9·0
Average	9·24	4·22	5·01	2·30	0·22	6·5	7·3

The alkalinity of the water-soluble ash was determined on the filtrate by titration with standard acid.

9. Soluble Silica Processes.

This process suggested by Zipperer, Matthes, and Müller (*Zeitsch. Untersuch. Nahrungs. Genussm.* 1906, **15**, 95), has been proved by Matthes and Rohdich (*Zeitsch. öft. Chem.*, 1908, **14**, 166) to be quite unreliable. They find that from the examination of twenty specimens of cacao beans the amount of soluble silica varies from 0·02 to 0·88 per cent.

10. Iodine Value of the Fat (Welman, *Zeitsch. öft. Chem.*, 1901, **7**, 500).

It has been suggested that the percentage of shell present in cocoa could be ascertained from the iodine value of the fat. As the range of iodine values for butter from nib overlaps the range for shell butter, this method is obviously useless, and becomes even ridiculous when we remember that nib contains 54 per cent. of butter and shell only 5 per cent.

11. Cold Water Extract.

It seemed probable that the cold water extract of cocoa would be much less than that of cacao shell. Actually they are almost identical if expressed on the fat-free, and this figure is useless for estimation of shell.

Germs.

Raw cacao beans contain 0·7 per cent. of "germs" (these are the hard rod-shaped radicles of the seed). As we have stated, the examples of nib and shell of which we give analyses are germ-free. Germs are usually very completely separated from the nib. In this separation some machines produce a residual containing up to 12 per cent. of germs. Hence, although the quantity of germs in cacao beans is small, shell is sometimes seen on the market containing a fair percentage of germs. The analytical figures for germs are therefore of interest in connection with the estimation of shell. The figures which we have obtained for germs are similar to those published by Richards (Analyst, 1918, **43**, 214): Moisture, 5·1 to 5·5; ether extract, 4·1 to 5·6

On fat-free dry material:

Nitrogen	6·1
Fibre	3·45
Ash	7·5 to 8·2
Soluble ash	4·2 „ 5·1
Alkalinity (as K_2O) of soluble ash ...	1·6

It will be noted that the presence of germs in added shell, if ignored, would cause one to under-estimate the amount of shell from either the nitrogen or fibre figure.

Conclusion.—We have seen that the chief difficulties in the way of an accurate determination of cacao shell are—(1) The natural variation in cacao shell due to botanic variety and to the distinctive treatment which the bean receives in each country; (2) that cacao shell is not a definite chemical substance, and hence the estimation can only be of a purely empirical character.

We have reviewed the various processes for estimating shell, and have concluded

that, with all its faults, the only one employed by itself which is capable of giving results of any value is the estimation of the crude fibre. It was reported in the ANALYST (1918, **43**, 205) that the method of estimating shell in cocoa was then receiving official consideration. We hope that the publication of our work may be found of assistance in any research which is being conducted. We find that there is no process which will determine so low a percentage as 5 per cent., but we consider that if the analyst deducts 8 per cent. from the shell percentage, as the mean of a number of analyses he finds by the fibre process, he may safely report that the cocoa contains at least the remainder.

In the Cocoa Powder Order, 1918, the amount of shell in cocoa powder was defined—Grade "A" to contain not more than 2 per cent. of shell, and Grade "B" not more than 5 per cent. of shell. It will be clear from the above that in our opinion no analytical method by itself, or in conjunction with others, will enable the analyst to distinguish between cocoa containing 2 per cent. and cocoa containing 5 per cent. of shell.

In conclusion, we should like to thank Mr. B. W. J. Warren, F.I.C., and Miss G. R. Woodhead, B.Sc., for their assistance.

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DISCUSSION.

Mr. P. A. ELLIS RICHARDS considered the authors were in rather a pessimistic vein in that they condemned all the recognised processes for the analysis of cocoa without suggesting an improved method. However, he quite agreed with them in the statement that when cocoa nib and shell were extremely finely ground the levigation process was of very little use. He himself preferred to base his conclusions as to the composition of a sample on a general consideration of all the analytical figures taken in conjunction with a full microscopical examination.

Mr. CRIBB said that he found himself in entire agreement with the main conclusion to which the authors of the paper had arrived—viz., that of all the methods suggested for the determination of the proportion of shell, the estimation of the fibre gave the nearest approximation to the truth; but at the same time he never thought it safe to express an opinion on one factor alone, and preferred to base his conclusions on as many other determinations as possible. Microscopic examination should, of course, never be omitted, as by it alone could the actual presence of shell be established.

In former days, when cocoa was less finely ground and also more uniform as regards the fineness of grinding, he had found that counting the particles of mucilage under the microscope, after staining with ruthenium red, afforded valuable quantitative indications, especially in the case of small proportions of shell. He found that, counting horizontally and vertically (near to the diameters) of a uniformly distributed and thin preparation under a $\frac{7}{8}$ inch cover-glass, that the number of particles in the case of shell was from 90 to 120, while in the case of good nib it rarely exceeded 4, and was often between 0 and 2. Of course, great care had to be taken to get the

preparations of uniform thickness. Now that the majority of cocoas are ground so much more finely, the method had lost much of its value, except that it gave a sure indication of the absence of shell when such was the case.

In view of the difficulty of obtaining ruthenium red, he had recently been employing methylene blue instead. It stained the mucilage well, but if the solution was too strong the starch and other structural elements were also coloured.

Where larger proportions of shell were present he had hoped that the estimation of the cocoa red would prove useful, as that substance was supposed to be entirely absent from the shell, but unfortunately his experience again coincided with that of the authors, as he also had obtained figures as high as 4·5 per cent. in the shell alone.

He inquired whether the authors had any knowledge as to the mucilage content of the shell of unripe as distinguished from ripe beans.

In reply, Mr. Knapp said: The various figures are all expressed on the dry fat-free material unless otherwise stated. The figures given on the cacao beans represent extremes that would be unlikely to occur with a manufactured cocoa, since this is always made from a mixture of beans. We agree with Mr. Cribb that the microscopic examination has a qualitative value, but we do not think that the average microscopist can obtain quantitative results. With regard to the ruthenium red test, this stains the mucilage, which occurs not in but on the seed-coat. I do not know if it is greater in amount on "unripe" beans, but would not be surprised to find it absent altogether from washed beans. The suggestion of sieving would be of use in certain cases if applied with discretion, but it was always possible that the shell might be finer than the cocoa or the cocoa finer than the shell, although we believe that if they were ground together the shell usually came out coarser than the cocoa.

THE ESTIMATION OF PHENACETIN AND OTHER PARA-AMINOPHENOL DERIVATIVES BY HYPOCHLOROUS ACID.

By A. D. POWELL.

(*Read at the Meeting, December* 4, 1918.)

The estimation of the substituted phenetidine compounds used in medicine, either alone or in admixture with other substances such as salol and caffeine, has always presented certain difficulties, and various methods have been proposed in recent years for the analysis of mixtures of these substances. Several of these are based on the varying solubilities of the compounds in organic solvents, a more or less complete separation being made, and the separated substances determined gravimetrically. Thus, Seidell (*J. Amer. Chem. Soc.*, 1907, **29**, 1088-1091; Analyst, 1907, **32**, 360) proposed a method of this type for the estimation of acetanilide, phenacetin, etc., in "headache powders." Emery, Spencer, and Le Febvre (*J. Ind. and Eng. Chem.*,

1915, **5**, 681-684; ANALYST, 1915, **40**, 445), for the estimation of phenacetin and salol, make use of selective hydrolysis, finally reconverting the phenetidine to phenacetin by acetylation, and weighing the phenacetin as such, the salol being estimated by bromine absorption. Another method recently published by Salkover (*Amer. J. Pharm.*, 1916, **88**, 484-485; ANALYST, 1917, **42**, 16) for the separation of these drugs depends on the solubility of salol in petroleum ether, phenacetin and acetanilide being nearly insoluble in this solvent.

Such methods suffer from the obvious defect that they do not sufficiently identify the substances present in the mixture, and the melting-points of the separated constituents cannot always be relied on, owing to the separation not being perfect.

Methods taking into account the chemical constitution of these compounds have also been proposed. Taylor and Vanderkleed (*Amer. J. Pharm.*, 1907, **79**, 151-156; ANALYST, 1907, **32**, 215), for instance, estimate phenacetin and acetanilide (individually), by steam distillation and titration of the acetic acid produced on hydrolysis. Another method proposed by Emery (*J. Ind. and Eng. Chem.*, 1914, **4**, 665-669; ANALYST, 1914, **39**, 433) for the separation and estimation of phenacetin and acetanilide depends on the property of phenacetin of combining with iodine to form an insoluble periodide, acetanilide either not reacting with iodine or producing a soluble compound. The amount of iodine precipitated from solution is determined by titration of the excess left in solution, and the phenacetin content calculated from the figures thus obtained. An iodimetric method for the estimation of phenolic compounds has been published by Wilkie (*J. Soc. Chem. Ind.*, 1911, **30**, 398; ANALYST, 1911, **36**, 294); but this does not appear to have been extended to the aminophenols and phenetidins, although it seems probable that such compounds might form definite iodo-derivatives.

As far as my own experience goes, however, no method has been published in which any characteristic reaction of *p*-phenetidine or *p*-aminophenol has been taken as the basis for the estimation of this group of compounds. The reactions of *p*-aminophenol with oxidising agents were therefore investigated, in order to determine which, if any, could be made the basis of a quantitative estimation. Oxidation by means of potassium dichromate to form quinone was tried, but was found unsatisfactory, as part of the *p*-aminophenol was converted to quinhydrone. The reaction between sodium hypochlorite and an acid solution of *p*-aminophenol was found to be much more promising. These substances react in accordance with the equation

$$OH.C_6H_4.NH_2HCl + 4Cl = O:C_6H_4:NCl + 4HCl,$$

the quinone chlorimine precipitating as golden-yellow flocks from concentrated solutions, but remaining in solution at dilutions below about 1 per cent.

P-phenetidine is also converted to quinone chlorimine by the action of hypochlorous acid. The reaction is quantitative, and provides a rapid means for the estimation of these bases and all their derivatives which yield the free base on hydrolysis.

The direct absorption of chlorine does not form a suitable basis for calculating the results, owing to the difficulty of determining when an excess has been added, and

it is therefore necessary to determine the amount of quinone chlorimine formed, after addition of excess of hypochlorite and removal of free chlorine from solution. In the absence of free chlorine, the reaction between the quinone compound and hydriodic acid affords a convenient means of determining this. The reaction is the reverse of that given above, four atoms of iodine being liberated by each molecule of quinone chlorimime, and *p*-aminophenol being re-formed.

As no reagent was found which will combine with the excess of free chlorine without also decomposing the chlorimine, and boiling is out of the question owing to the volatility and instability of the latter in hot solutions, the chlorine must be removed by blowing a current of air through the solution. Experiments showed that chlorine is fairly rapidly removed by this means, 100 c.c. of a saturated aqueous solution of this gas losing 98 per cent. of its strength after five minutes aeration at the rate of 700 to 800 c.c. of air per minute, and becoming practically free from chlorine after fifteen minutes. The quinone chlorimine being also slightly volatile, and tending to decompose on long standing in acid solution, it is necessary to add a small correction to account for this. Any error introduced by the action of the dissolved air on the iodide subsequently added is included in this correction, which averages 1·5 per cent. of the total quinone chlorimine present for an aeration of from fifteen to twenty minutes.

The details of the method finally adopted are shown in the following examples of its application:

ESTIMATION OF *p*-AMINOPHENOL, *p*-PHENETIDINE, etc.—An amount of an acid solution equivalent to about 0·1 grm. of the base is measured into a 250 c.c. stoppered bottle and diluted to rather more than 100 c.c.; 5 c.c. of strong hydrochloric acid are added, followed by 10 c.c. of sodium hypochlorite solution (about 0·8 N). The resulting solution should be pure yellow, and not deposit yellow flocks. Air is now blown through at a brisk rate for fifteen minutes, in which time all chlorine will have been removed, 2·5 grms. of potassium iodide are added, and the solution allowed to stand for at least five minutes, as the reduction is rather slow. The liberated iodine is then titrated with $\frac{N}{10}$ thiosulphate and starch indicator. Any residual blue tint shows that reduction has not been complete.

Each c.c. of $\frac{N}{10}$ thiosulphate is equivalent to 0·00273 grm. of *p*-aminophenol, or 0·00343 grm. of *p*-phenetidine. The result is multiplied by the factor 1·015 to correct for loss during aeration.

ESTIMATION OF PHENACETIN.—One grm. of phenacetin is boiled for two hours with a mixture of 25 c.c. strong hydrochloric acid (1·16) and 15 c.c. water in a small flask fitted with an air condenser. After cooling, the solution is diluted to some definite volume, and an aliquot representing 0·2 grm. phenacetin is taken for estimation exactly as above.

Each c.c. of $\frac{N}{10}$ thiosulphate is equivalent to 0·00448 grm. of phenacetin. A large number of samples of commercially pure phenacetin, examined as above, gave figures ranging from 99·2 to 100·2 per cent.

ESTIMATION OF PHENACETIN IN ADMIXTURE.—The following experiments were made on mixtures of phenacetin with caffeine citrate, salol, and acetanilide respectively:

With Caffeine Citrate.—A mixture of 0·8 grm. phenacetin with 0·4 grm. caffeine citrate was treated exactly as for phenacetin. The results were slightly high, owing to formation of a small amount of some substance from the caffeine citrate which liberated iodine from hydriodic acid. The percentage of phenacetin calculated out 68·5 and 68·7, instead of 66·7 required by theory. No correction for the volatility of the quinone chlorimine was made in these cases, the error already mentioned more than compensating for loss by this means.

With Salol.—A mixture of equal parts of phenacetin and salol (0·5 grm. of each) was dissolved in 20 c.c. 10 per cent. sodium hydroxide, and warmed on the steam-bath for fifteen minutes to hydrolyse the salol; 40 c.c. of strong hydrochloric acid were then added, and the mixture boiled for two hours. The hydrolysed solution was shaken with ether to remove salicylic acid and phenol, and the chlorination and titration carried out in the usual manner. The amount of phenacetin found was 49·3 per cent. It was found necessary to remove the products of hydrolysis of salol before adding the hypochlorite, as the precipitates they formed with this reagent held back chlorine and caused high results to be obtained.

With Acetanilide.—Mixtures of acetanilide and phenacetin cannot be analysed without first removing the acetanilide, as the aniline produced from this substance forms an oily precipitate which apparently retains free chlorine.

ESTIMATION OF OTHER *p*-PHENETIDINE OR *p*-AMINOPHENOL DERIVATIVES.—Lactophenin (lactyl-*p*-phenetidine) and salophen (salicylic ester of acetyl-*p*-amino-phenol) were both estimated after hydrolysis in exactly the same manner as phenacetin, lactophenin giving 99·3 per cent. and salophen 100·4 per cent., after adding the correction previously mentioned.

ANALYSIS OF PHOTOGRAPHIC DEVELOPERS.—In addition to the medicinal substances already mentioned, there are several *p*-aminophenol derivatives largely used in photography as developers, which may be estimated in the same manner. For instance, in a developer of the rhodinal type, the proportion of *p*-aminophenol may be quickly found by direct treatment of the acidified solution, the sulphite present being oxidised by the excess of chlorine added.

In the case of metol (methyl-*p*-aminophenol sulphate) it is interesting to note that, owing to the presence of the methyl group in the amino-group, no chlorination of the latter takes place, although a quinone derivative is formed. The reaction is probably

$$OH.C_6H_4.NH.CH_3 + 2Cl = O:C_6H_4:N(CH_3) + 2HCl.$$

Consequently, in the subsequent oxidation of hydriodic acid, only two atoms of iodine are liberated per molecule instead of four, as in the case of *p*-aminophenol. The reaction therefore provides a simple means of distinguishing between metol and 'metol substitutes," as all the substitutes that I have examined have proved to be either *p*-aminophenol or *p*-aminocresol salts, none of them showing evidence of the presence of a methyl group substituted in the amino group, when tested by the quinone chlorimine method.

I desire to express my thanks to Messrs. Boots' Pure Drug Company, in whose laboratories the above work was carried out.

NOTES.

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.

ESTIMATION OF SMALL QUANTITIES OF ETHYL ETHER IN ETHYL ALCOHOL.

SEVERAL good methods are available for the estimation of alcohol in ether, but the converse problem is not often met with and presents considerable difficulty, and no method appears to have been published for quantities of the order of 1 per cent.

The method of Fleischer and Frank (*Chem. Zeit.*, 1907, **31**, 665) and of Wolff (*ibid.*, 1910, **34**, 1193) are not suitable for very small quantities.

Density determinations yield fairly satisfactory results, but the experimental errors are necessarily rather large, as one is concerned with units in the fourth and fifth decimal place. When dry ether is mixed with alcohol a very slight diminution in volume takes place; with equal volumes this diminution amounts to 0·5 per cent. of the total volume. For small quantities it is negligible. The density of ethyl ether, $D\ \frac{15\cdot0}{15\cdot0}$ is 0·7198 (Wade and Finnemore), and of absolute alcohol at the same temperature is 0·7943; so that each 1 per cent. of ether lowers the density of alcohol by 0·0007. The presence of 0·25 per cent. of water will mask the effect of one per cent. of ether; and as 100 per cent. alcohol is very rarely met with, it is not sufficient merely to determine the density and refer to a table.

Alcohol of 99 per cent. and upwards distils over unchanged under ordinary conditions; any ether it contains passes over in the first fractions, and no constant boiling mixture is formed. It is therefore possible to estimate the amount of ether by the determination of density before and after distillation. The density of the alcohol is taken as that obtained after the removal of the ether. The amount of ether is then indicated by the expression— $\frac{D\ (\text{alcohol}) - D\ (\text{mixture})}{0\cdot0007}$.

The following tables show the effect of ether on the density of alcohol. The ether was dry and free from alcohol, and had $D\ \frac{15\cdot6}{15\cdot6}$, 0·72087. The alcohol was of $D\ \frac{15\cdot6}{15\cdot6}$ 0·79530 (= 99·46 per cent. by weight.)

TABLE I.

Per Cent. Ether.	$D\ \frac{15\cdot6}{15\cdot6}$.	Difference.	Per Cent. Ether Found.
0·10	0·79522	0·00008	0·11
0·35	0·79505	0·00025	0·36
0·58	0·79494	0·00036	0·51
1·33	0·79435	0·00095	1·36
1·65	0·79416	0·00114	1·63
2·53	0·79380	0·00150	2·14

TABLE II.

Per Cent. Ether.	$D\frac{15\cdot6}{15\cdot6}$.	Difference.	Per Cent. Ether Found.
0·00	0·79421	—	—
0·45	0·79394	0·00027	0·39
0·78	0·79370	0·00051	0·73
1·09	0·79355	0·00066	0·94

The densities were determined in a pyknometer of the Perkin type fitted with glass caps. The results in Table II. are with a stronger absolute alcohol (99·80 per cent. by weight). The figures show that the ether can be determined within the limits of error of density determinations. When distillation is necessary, the error becomes larger. The following experiments were made using a Young's rod and disc still-head and a double-surface condenser. A calcium chloride guard tube is essential, and the receiver should be cooled in a freezing mixture.

EXPERIMENT I. Ether added, 1·14 per cent.; weight taken, 158 grms.

Fractions.	Weight.	Density.	= Per Cent. Ether.
1	15·544	0·79014	0·90
2	17·693	0·79602	0·06
3	14·842	0·79643	—
4	17·344	0·79644	—
5	15·502	0·79642	—
		Total ether found = 0·96 per cent.	

EXPERIMENT II: Ether added, 1·05 per cent.; found, 0·88 per cent.
EXPERIMENT III: Ether added, 0·28 per cent.; found, 0·13 per cent.
The amount of sample taken was 20 and 80 grms. respectively.

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ESTIMATION OF SILICA AND SAND.

The analyst is sometimes called on to differentiate between "sand" and silica forming a component of vegetable tissues in feeding stuffs. A recent inquiry led me to find with surprise that no text-book which happened to be available for reference gave any directions. Some readers may, therefore, perhaps care to know the procedure which I have myself found useful.

Two portions (2 grms. each) of the feeding stuff are slowly incinerated at a low temperature (to avoid fusion) over an Argand burner. One portion is boiled with 10 c.c. of dilute (20 per cent.) hydrochloric acid, and the insoluble matter is filtered off, incinerated, and weighed, giving the total silica, including sand. The other portion of ash is boiled in the capsule with 10 c.c. of a 10 per cent. solution of sodium hydroxide. After dilution the insoluble matter is filtered off, washed, burnt, digested

with hydrochloric acid, and the insoluble silica filtered off, burnt, and weighed, being taken as the "sand," as distinguished from "natural silica."

Recently I made the following experiment: Two portions of wheat straw of 2 grms. each gave ash—(*a*) 7·90 per cent. and (*b*) 7·95 per cent. The ash from portion (*a*) was treated successively with soda and acid as just described, and gave 0·95 per cent. of undissolved silica or "sand." The ash from portion (*b*) digested with hydrochloric acid alone gave 5·85 per cent. of total silica. This, when boiled with sodium hydroxide and washed with HCl, gave 0·80 per cent. of "sand." Apparently, therefore, it is preferable to apply the soda digestion to the total siliceous matter after freeing from other ash constituents by acid treatment. In soil I have found 98 per cent. of the total siliceous matter to remain undissolved by successive acid and alkali treatment as above, while of the total siliceous matter of straw 86 per cent. is dissolved, so that this method may be regarded as fairly distinguishing between plant silica and the "sand" of soil.

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ESTIMATION OF SILICA AND SAND.

I have read Mr. Lloyd's note, and may perhaps be allowed to supplement it. From time to time I have had occasion to attempt a quantitative discrimination between sand and "natural" silica in Indian rice-bran. Rice-bran usually contains some proportion (which should be small, but is sometimes large) of rice shudes or husks, which contain a large quantity of natural silica, more than 20 per cent. of their own weight. For this purpose I have used, not caustic soda, as used by Mr. Lloyd, but a 10 per cent. solution of sodium carbonate. The total siliceous matter (insoluble in boiling dilute hydrochloric acid) is weighed and boiled with 100 c.c. of the sodium carbonate solution, filtered, washed, burnt and weighed. I have found this mode of treatment to dissolve 91 per cent. of the natural silica of the rice-husks and only about 5 per cent. of "sand" or silica in fine earth. Hence, if A = total siliceous matter insoluble in acid, and if B = the siliceous matters not redissolved by the treatment of sodium carbonate, then

$$\text{Percentage of sand} = \frac{B - 0{\cdot}09A}{0{\cdot}86}$$

This approximately corrects the cross-errors otherwise due to the incompletness of the solvent action of the soda on the silica of the plant tissues, and to its small but appreciable action on the adventitious silica present in the form of sand or clay.

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NOTATION.

In many cases in the determination of the acidity or alkalinity of foods the nature of the acid or base may not be known, or several may be present. In such cases it is convenient, in recording the result of the analysis, to make a quantitative statement of the *fact* apart from any *theory* as to the nature of the reacting substance. I have used the following notation for some time; it is both concise and definite:

$$\text{Flour} \begin{cases} \text{Alkalinity of ash } 2{\cdot}1 \text{ N v/w.} \\ \text{Acidity (methyl red)} = 2{\cdot}0 \ \frac{N}{10} \text{ v/w.} \end{cases}$$

This means that the alkalinity of the ash of the flour in question was equivalent to 2·1 c.c. of $\frac{N}{1}$ alkali per 100 grms. of flour, and that the acidity of the flour to methyl red was equivalent to 2·0 c.c. of $\frac{N}{10}$ acid per 100 grms. of flour, the symbol

v/w (*i.e.*, volume on weight) indicating c.c. per 100 grms. Multiplication by the appropriate volumetric factor will, if required, convert the figure into a percentage of a particular acid or alkali. In the first case multiplication by 0·047 will give 0·1 per cent. K_2O.

A corresponding notation is sometimes useful for liquids; for instance:

Effluent: acidity = 2·9 $\frac{N}{10}$ v/v.

Water: alkalinity { (phenolphthaleïn) 0·5 $\frac{N}{100}$ v/v. (methyl red) 3 $\frac{N}{100}$ v/v.

In the first case 100 c.c. of the effluent had an acidity equivalent to 2·9 c.c. $\frac{N}{10}$ acid.

This notation is in accordance with my suggestion (ANALYST, 1897, **22**, 89) that w/v (*i.e.*, weight on volume) should be used to indicate grms. per 100 c.c., and v/v—*i.e.*, volume on volume—c.c. per 100 c.c.

J. F. LIVERSEEGE.

BIRMINGHAM.

VOLUMETRIC DETERMINATION OF BARIUM.

In connection with Dr. Waddell's interesting paper (ANALYST, 1918, **43**, 287), might I suggest the use of water saturated with barium chromate for washing the precipitate? This is better than applying a correction for the solubility in water. This is the plan which I have long followed in the estimation of magnesia as pyrophosphate; the precipitate before ignition is washed with dilute ammonia-saturated with ammonium-magnesium-phosphate.

THOS. STEEL.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

New Method for the Analysis of Butter. P. Erculisse and H. Dackweiler. (*Ann. Chim. anal.*, 1918, **23**, 225-234.)—The authors determine the saponification value, the "silver" value, and the "magnesium" value of the fat. The saponification value is determined on 4 grms. of the fat, and the resulting soap is then diluted to a definite volume. A portion of this solution is treated with excess of $\frac{N}{10}$ silver nitrate solution, the solution filtered, and the excess of silver titrated in the filtrate all the fatty acids, with the exception of butyric acid, are precipitated, so the difference between the saponification value and the amount of silver used for the precipitation gives the measure of the butyric acid present—*i.e.* the "silver" value. Expressed in c.c. of $\frac{N}{10}$ solution per 5 grms. of fat, the "silver" value is similar to the Reichert-Meissl value. The "magnesium" value is determined by treating a further portion of the soap solution with magnesium sulphate which precipitates all acids higher than C_{12}, filtering the mixture and determining the amount of silver nitrate required to precipitate the fatty acids other than butyric acid in the filtrate. The "magnesium" value, calculated to 5 grms. of fat, corresponds with the Polenske

value. It is claimed that the methods are more reliable than the ordinary Reichert-Meissl and Polenske processes. The analysis of one sample of butter is recorded.

W. P. S.

Coffee Preparations for French Army Use. M. Balland. (*Compt. rend.*, 1918, **167**, 423-425.)—Both before and during the war numerous coffee preparations, for use in the French Army, have been under consideration, among them liquid extracts of varying thickness containing 60 to 80 per cent. of water. Some of these contain as much as 50 per cent. of caramel, and many of them 12 to 15 per cent. of alcohol. They are usually put up in powder form in metal boxes; these extracts are hygroscopic, and become sticky when exposed to the air, dissolving readily in cold water. One of these contained 2 per cent. of water, 18 per cent. of ash, and 80 per cent. of sugar-free extractives, of which 8·5 per cent. was nitrogenous matter; caffeine was present, but only traces of fat and essential oil. Tablet preparations covered with tinfoil are usually put up in 10 grm. portions, and are hygroscopic and soluble in water; they usually consist of 88 to 90 per cent. of sugar, 10 to 12 per cent. of extract, and 3 or 4 per cent. of water. Some of these preparations have had to be discarded for Army use, owing to their acquiring a bitter flavour after some months, and it has been found that the aroma is better preserved without the use of sugar. A novel method of roasting the beans after a preliminary grinding in the green state was claimed to effect great economies, but was unfavourably reported upon by a specially appointed Commission.

Coffee Shells or Cuticles.—About 0·35 per cent. of shell or husk usually separates during the roasting of coffee. This material contains much inert cellulose and gives an infusion of poor quality, but there is no need, as has been suggested, to separate this husk from the rest of the roasted coffee. The following figures illustrate the relative composition of coffee and husk:

	Coffee Santos (Roasted).	Shell detached from this Coffee while Roasting.	Another Sample of Shell.
Moisture	3·0	5·6	5·9
Nitrogenous matter	14·4	17·4	16·0
Fat	12·5	8·1	8·1
Extractives (by difference) ...	51·8	26·5	15·5
Cellulose	13·6	34·5	36·0
Ash	4·7	7·7	18·5
	100	100	100
Caffeine	1·3	0·69	0·49
Aqueous extract	26·0	18·2	18·0

The employment of coffee substitutes is not permitted in the French Army, the reserves of Brazilian and Colonial coffee having proved sufficient. Apart from the well-known chicory, the three following substitutes are worthy of note, especially the

the last; (1) A brown powder consisting of a mixture of roasted wheat and barley; (2) a powdered black material, made from roasted figs; (3) roasted Soya bean.

	1.	2.	3.
Moisture	8·9	7·2	4·9
Nitrogenous matter	12·6	8·9	45·6
Fat	1·3	3·5	21·7
Sugar	3·9	15·9	3·1
Extractives (by difference) ...	71·5	59·7	19·5
Ash	1·8	4·8	5·2
	100	100	100
Aqueous extract ...	54·2	41·4	19

H. F. E. H.

Estimation of Lactose. E. Hildt. (*Comptes rend.*, 1918, **167**, 756-759.)—Direct estimation of lactose in milk by titration against Fehling's solution is untrustworthy in cases where the milk has undergone decomposition or has been preserved with dichromate, as the lactose is hydrolysed partially into dextrose and galactose, and, consequently, the usual lactose factor of the Fehling's solution cannot be used in calculating the amount of the sugar present. The author recommends the complete hydrolysis of the lactose before the titration. Mineral acids are unsuitable for the purpose, but certain benzene and naphthalene sulphonic acids, etc., yield good results; it is better to use the barium or sodium salts of these acids together with an equivalent of sulphuric acid. The lactose solution to be hydrolysed should contain 0·5 per cent. of the sugar and 1 per cent. of the sulphonic acid, and the mixture should be heated at 100° C. for four hours. Ten c.c. of Fehling's solution is equivalent to 0·0506 grm. of hydrolysed lactose or 0·0708 grm. of hydrated lactose. W. P. S.

Estimation of Lactose in Milks heated after the Addition of Sodium Bicarbonate. C. Porcher and A. Bonis. (*Ann. Falsificat.*, 1918, **11**, 295-299.)—When milk containing 1 grm. per litre of sodium bicarbonate is heated in an autoclave at 120°C., the reducing power of the lactose is less affected than the optical rotation, which is considerately lowered. For example, a sample of raw milk containing 45·7 grms. per litre of lactose showed, after heating for twenty minutes with sodium bicarbonate, 44·0 grms. by reduction and 31·2 grms. by the polarimeter. This has been shown to be due to the formation of lævorotatory products from the lactose, and there is no need to adopt Jensen's explanation that the reduction in the optical rotation of lactose is caused by the formation of lævorotatory nitrogenous products from the casein. C. A. M.

French Table Mustard. P. Carles. (*Ann. Falsificat.*, 1918, **11**, 310-316.)—The old type of French table mustard was made by mixing the mustard with the juice of

ripe grapes, but at the present time most manufacturers use vinegar as the medium. Eleven commercial samples had the following composition: Water, 62·5 to 75·0; total ash, 2·5 to 11·30; soluble ash, 1·0 to 9·55; sodium chloride, 0·66 to 7·25; potassium oxide, 0·08 to 0·25; allyl mustard oil, 0·056 to 0·257; total acidity, 1·84 to 4·80; and acetic acid, 0·5 to 3·5 per cent. C. A. M.

Detection of Added Water in Wine. U. Pratolongo. (*Staz. sperim. agrar. ital.*, 1918, **51**, 56-60; through *Internat. Rev. Sci. Pract. Agric.*, 1918, **9**, 1104.)—The method is based on the fact that natural wine forms a saturated solution of potassium hydrogen tartrate and calcium tartrate. If, therefore, a wine dissolves further quantities of these salts the presence of added water is indicated. Suitable quantities of the wine are treated separately with an excess of potassium hydrogen tartrate and calcium tartrate, the mixtures are kept at 50 to 60° C. for thirty minutes, then cooled, the undissolved salts are separated, and the total tartaric acid and total calcium are estimated. Estimations of these constituents are also made in the original wine. The method will show the presence of as little as 5 per cent. of added water, and the amount of the latter may be calculated when it varies from 5 to 20 per cent. The test does not permit of the detection of water added to the must. W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Marine Animal Oils from the Antarctic. (*Bull. Imp. Inst.*, 1918, **16**, 140-145.)—Five samples of sea-leopard oil, seven of seal oil and two of penguin oil, have been examined, with the following results:

Oils.		Sp. Gr. 15°/15°.	Saponification Value.	Iodine Value.	Solidifying Point of Fatty Acids.
Sea leopard	Maximum	0·925	195·1	127·5	11·9° C.
	Minimum	0·924	193·7	119·7	3° C. to 4° C.
	Average	0·9245	194·4	123·8	—
Weddell seal	Maximum	0·931	201·5	147·8	19° C.
	Minimum	0·924	192·0	122·1	16° C. to 17° C.
	Average	0·9275	195·1	134·6	—
Penguin ...	Average	0·932	197·5	126·9	31·4° C.

The penguin oil as received was a brownish-yellow, cloudy, viscous oil containing a considerable amount of stearin and having a fishy odour. All the samples were fairly light in colour and free from appreciable amounts of dirt or water. The acid values were low (averaging 1·5). All the oils on examination by experts were stated to be suitable for soap-making, and yielded much glycerol. The penguin oil was of less commercial value than the seal and sea-leopard, being darker and thicker. When filtered, the oils could be used for colliery lamps, tempering steel, leather-dressing, and other purposes. H. F. E. H.

Bacterial Precipitins and the Detection of *B. botulinus* in Preserved Foods by the Thermo-Precipitation Method. M. Bornand. (*Trav. chim. aliment. hyg.*, 1918, **9**, 87-98; through *Internat. Rev. Sci. Pract. Agric.*, 1918, **9**, 1113-1114.)—The thermo-precipitin method, first described by Ascoli and Valenti, consists in placing a few grms. of the material, supposed to be infected (with anthrax), in physiological salt solution and heating the mixture for five minutes in a boiling water-bath; after cooling, the mixture is filtered, and the filtrate is placed in contact with the precipitating serum. If the material examined is infected, a white ring forms within one hour at the point of contact of the two liquids. The precipitating serum used in applying this method to the detection of *B. botulinus* in preserved foods is prepared by inoculating a rabbit with extracts of a culture of the bacterium, the subcutaneous injections being made in both thighs at intervals of three or four days. Eight days after the last injection the animal is bled and the serum preserved with toluene. Samples of preserved beef and herrings infected with the bacterium gave distinct precipitates with the serum, but the reaction was negative in the case of infected preserved vegetables. W. P. S.

ORGANIC ANALYSIS.

Tobacco from Ceylon. (*Bull. Imp. Inst.*, 1918, **16**, 149-159.)—Further samples of experimental tobacco growths from Ceylon have been received (ANALYST, 1912, **37**, 500) and examined at the Imperial Institute. Twenty-six samples were received in 1915, and of these none was considered by experts really suitable for the English market, since all had a pungent and unpleasant flavour when smoked. Their nicotine content varied from 1·7 to 4 per cent. (average, 2·6 per cent.) on a 14 per cent. moisture basis, and the nitrogen from 1·9 to 3·2 per cent. (average 2·5 per cent.). All the samples were grown in the same locality, and had been air-cured, but the potash content of the ash varied from 6·7 to 22·7 per cent., while chlorides were excessive in all—a fault characteristic of Ceylon tobaccos. A further five samples were received in 1917, four of which were White Burley and one from imported Turkish seed. The White Burley is of much better quality to that previously received, and was valued at from 9d. to 1s. per pound. The burning properties were fair, but there was almost entire absence of pleasant flavour. A bulk sample gave the following results: Moisture, 14 per cent.; nicotine, 4·6 per cent.; nitrogen, 3·4 per cent.; ash, 19 per cent. An analysis of the ash showed lime, 34·7 per cent.; soda, 2·5 per cent.; SO_3, 3·5 per cent.; Cl, 14·2 per cent.; CO_2, 15·8 per cent.

The sample grown from Turkish seed was of inferior appearance, did not burn well, but had a fairly good flavour and Turkish aroma. H. F. E. H.

Determination of the Adhesiveness of Glue. M. Rudeloff. (*Mitt. K. M. Materialpruf.*, 1918, **36**, 2-49; through *J. Soc. Chem. Ind.*, 1918, **37**, 743A.)—The solution of the glue is applied to the planed end surfaces of two pieces of red beech wood 185 mm. long, 125 mm. broad, and 50 mm. thick, and these are placed so that the glued surfaces cross at right angles. The glue film is then allowed to dry under definite pressure, and the force required to tear the pieces of wood apart is measured

by means of a suitable machine. In a series of determinations made in this way it was found that for glue solutions up to 200 per cent. of water (referred to weight of glue dried at 100° C.) the tenacity of the film decreased in proportion to the extent to which the wood was heated prior to glueing, but that in the case of solutions with 300 per cent. of water the greater degree of heating had a favourable influence. The tenacity of the glue film does not decrease in direct proportion to the rise in the amount of water. In the case of solutions with 100 to 150 per cent. of water the pressure under which the glue film is dried has no appreciable influence on the tenacity of the film, but with higher amounts of water the drying pressure has considerable influence, especially when the wood has been previously heated. The most suitable conditions for testing samples of glue by this method are the use of solutions containing 150 per cent. of water, previous heating of the pieces of wood to 40° C. in dry air, and drying of the film under a pressure of not less than 0·84 kilo per sq. cm. Solutions containing 100 to 150 per cent. of water give concordant results by this method, which may also be used for comparison with the results obtained by determining the viscosity at 35° C. of glue solutions with 556 per cent. of water.

INORGANIC ANALYSIS.

Alkali Iodides as Reagents for Cadmium and Nickel. A. Agrestini. (*Gazz. Chim. Ital.*, 1918, **48**, 30-34.)—On treating an ammoniacal solution of a cadmium salt with a 20 to 30 per cent. solution of potassium iodide, a white crystalline precipitate, $Cd(NH_3)_2I_2$, is obtained. Under similar conditions nickel salts yield a bluish-violet precipitate, $Ni(NH_3)_6I_2$. The test may be used for the detection of nickel in the presence of cobalt. For this purpose the solution of the mixed salts is boiled for three to four minutes with excess of ammonia and hydrogen peroxide, cooled, and filtered. The filtrate is then treated with potassium iodide solution and a few drops of ammonia solution, the cobaltamine not giving any precipitate with alkali iodides. Or the cobalt may be removed by precipitation as cobalt-potassium nitrite; or the solution may be treated with a strong solution of ammonium thiocyanate, and shaken in a separating funnel with a mixture of 1 part of amyl alcohol and 10 parts of ether, which dissolves the ammonium cobalti-thiocyanate. After two more extractions the test is applied to the residual aqueous layer. Alkali bromides form analogous compounds with nickel and cobalt, but do not give any appreciable precipitate with an ammoniacal solution of cadmium. C. A. M.

Electrolytic Estimation of Metals without the Use of External Electric Energy. M. François. (*Comptes rend.*, 1918, **167**, 725-727.)—A piece of conductive metal—*e.g.*, nickel—about 0·5 mm. thick, 60 mm. long, and 12 mm. wide, is placed across a platinum crucible containing 20 c.c. of 10 per cent. sulphuric acid and 0·5 grm. of potassium iodide, and a cylindrical rod of pure zinc 5 mm. in diameter and 40 mm. long is fixed by means of a notch in an opening in the nickel foil, so that its other end is suspended in the acid. If a mercury salt is then introduced, the mercury will be deposited on the interior of the crucible, and not upon the zinc. To prevent irregularities due to the formation of small electric couples by impurities in the zinc,

the latter should be amalgamated about twenty-four hours before use, and covered with a porous membrane of filter-paper tied on with cotton. The deposition of the mercury is complete in twenty-four hours. For the estimation of gold or silver the sulphuric acid is replaced by 2 c.c. of water to dissolve the gold or silver salt; 9 c.c. of a 10 per cent. solution of potassium cyanide; 5 c.c. of potassium hydroxide solution (sp. gr. 1·332); and 2 c.c. of ammonia solution (sp. gr. 0·924). C. A. M.

Detection of Hydrochloric Acid in the Presence of Bromic and Iodic Acids. H. Purgotti. (*Gazz. Chim. Ital.*, 1918, **48**, 63-66.)—The solution is treated with silver nitrate, and the precipitate washed with nitric acid and digested for a few minutes with a solution of an alkali hydroxide. This will convert the silver bromate or iodate into the corresponding alkali salts, and these may be detected in the filtrate by adding excess of hydrochloric acid and 1 to 2 c.c. of carbon bisulphide, and shaking the liquid, after cautious addition of a drop or two of sulphurous acid solution. For a quantitative estimation the filtrate is reduced by means of zinc or aluminium powder, and the resulting bromide or iodide precipitated with silver nitrate. C. A. M.

Detection and Estimation of Hydrogen Phosphide in Hydrogen. J. Soyer. (*Ann. Chim. anal.*, 1918, **23**, 221-225.)—Hydrogen used for aeronautical purposes and prepared by the action of sodium hydroxide on ferrosilicon always contains traces of hydrogen phosphide, the quantity varying from 1 volume in 15,000 to 1 volume in 40,000, or less. The hydrogen phosphide is an objectionable constituent on account of its toxicity and its action on balloon fabric. To detect its presence the hydrogen is burned from a platinum jet and the flame directed against the edge of a porcelain basin; hydrogen phosphide imparts a characteristic green colour to the flame; the latter also exhibits the spectrum of phosphorus. If a drop of water on a glass rod is held in the flame for fifteen seconds and then tested with molybdic acid reagent, a yellow precipitate is obtained. The quantity of hydrogen phosphide present is estimated by passing from 2 to 20 litres of the hydrogen, together with a large excess of air, through a silicon combustion tube; the latter is inclined slightly, and the upper end, where the hydrogen enters through a platinum jet, is heated to bright redness, whilst the lower end is cooled and connected with absorption vessels containing water. About 20 litres of the gas may be burnt in one hour. At the end of the operation the contents of the absorption vessels are transferred to a beaker, the combustion tube is rinsed with water and the rinsings added to the beaker, the solution is treated with 5 grms. of ammonium nitrate, evaporated to a small volume, and the phosphoric acid precipitated with molybdic acid. The precipitate is collected and weighed, or, if very small, its quantity is estimated colorimetrically. W. P. S.

Iodotannic Reagent (Estimation of Alkali in Very Low Concentrations). D. E. Tsakalotos and D. Dalmas. (*Bull. Soc. Chim.*, 1918, [iv], **23**, 391-400.)—The reagent consists of 1 c.c. of strictly $\frac{N}{10}$ and neutral iodine solution and 1 c.c. of a 1 per cent. solution of tannin. The two solutions are mixed in a porcelain dish

immediately before each test. The solution to be tested is then run in from a burette. At first the orange colour of the solution merely becomes fainter, whilst a red colouration produced in the neighbourhood of the drops falling from the burette disappears on stirring. After addition of sufficient of the solution under examination, however, a persistent red tinge appears, and this increases with further additions. From this point onwards the solution is tested after each addition by bringing a drop on to a piece of starch paper, and the titration may be completed in this way, the end-point being shown by the non-appearance of the iodine reaction; but more exact results are obtained by adding 5 c.c. of starch solution to the mixture itself, when the starch paper shows that the end-point is almost reached. Of the purest distilled water obtainable, 211 c.c. sufficed to bring about the disappearance of the starch iodide reaction. Of $\frac{N}{100}$ alkali (sodium hydroxide, potassium hydroxide or carbonate, calcium hydroxide or ammonia) precisely 9·7 c.c. sufficed to bring about the disappearance of the starch iodide reaction. Of $\frac{N}{200}$ alkali 18·5 c.c. sufficed, of $\frac{N}{1000}$ alkali 72 c.c., and of $\frac{N}{10000}$ alkali 170 c.c. These volumes are not inversely proportional to the normality of the solutions, but show that the more dilute solutions behave precisely as might be expected if they are regarded as mixtures of $\frac{N}{100}$ alkali with varying quantities of water which is not without effect on the reagent. The above data will enable anyone to make use of the method for the estimation of concentrations of alkali of the order of $\frac{N}{10000}$, for which purpose titration with acid and indicators is useless. The authors demonstrate the application of their principle very lucidly, but their printer has transposed two columns of an important table, and the unit of alkalinity throughout the author's argument is the French unit of hardness. G. C. J.

Estimation of Nitrates and Nitrites. W. Strecker. (*Ber.*, 1918, **51**, 997-1004; through *J. Soc. Chem. Ind.*, 1918, **37**, 578A.)—The solution to be analysed, containing nitrites and nitrates equivalent to not more than 0·11 grm. $NaNO_2$ and 0·18 grm. KNO_3, is dropped into a boiling concentrated solution of ammonium chloride, at least 100 times as much of this salt being taken as there is nitrite present, the solution being in a flask which is connected with an apparatus for making air-free carbon dioxide on the one hand, and a water-cooled Schiff's nitrometer, containing potassium hydroxide, on the other. After adjusting the pressure and noting the volume of nitrogen, a solution of iron in concentrated hydrochloric acid is introduced into the flask and the nitric oxide is collected.

Analysis of Molybdenum Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour. P. Jannasch and O. Laubi. (*J. prakt. Chem.*, 1918, **97**, 154-181; through *J. Soc. Chem. Ind.*, 1918, **37**, 732A.)—The substance, such as molybdic acid, molybdates, molybdenum ores, etc., is heated in a current of carbon dioxide saturated with carbon tetrachloride vapour; the molybdic acid volatilises and is collected in a receiver, then evaporated with nitric acid, ignited, and weighed. To determine molybdenum, 0·4 grm. of the sample is heated at 430° to 630° C. in the carbon dioxide-carbon tetrachloride vapour, and the volatilised substances collected in a suitable receiver; a trace of substance may remain

unvolatilised, and this may be heated with hydrochloric acid, the solution filtered, and the filtrate added to the contents of the receiver, which are then evaporated. After silica has been separated in the usual way, the solution is heated with an excess of ammonia, the ferric hydroxide collected on a filter, and the filtrate evaporated to dryness with the addition of *agua regia ;* the residue of molybdic acid thus obtained still contains traces of silica, and is once more volatilised in a current of carbon tetrachloride.

Analysis of Tungsten Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour. P. Jannasch and R. Leiste. (*J. prakt. Chem.*, 1918, **97**, 141-153 ; through *J. Soc. Chem. Ind.*, 1918, **37**, 732A.)—The method depends on the formation of a mixture of volatile chlorine derivatives of tungsten when tungstic acid or a tungstate is heated in a current of carbon dioxide saturated with carbon tetrachloride vapour. The volatilised compounds are decomposed by the dilute acids and the tungstic acid precipitated in a weighable form. A temperature below red heat is required for the volatilisation, which takes about 1 hour for completion. The method may be used for the determination of tungsten in scheelite and woframite.

Analysis of Vanadium Compounds with the Aid of Carbon Tetrachloride. P. Jannasch and H. E. Harwood. (*J. prakt. Chem.*, 1918, **97**, 93-137 ; through *J. Soc. Chem. Ind.*, 1918, **37**, 578A.)—Vanadium in various vanadium compounds can be estimated by heating the latter in a current of carbon dioxide and carbon tetrachloride vapour. The compound is placed in a silica boat inside a silica tube, and the resulting volatile vanadium oxychloride and the tetrachloride are collected by passage into two receivers containing dilute nitric acid and water respectively. The resulting solution of vanadic acid is evaporated to dryness, the residue being subsequently dissolved in dilute sulphuric acid, treated with a slight excess of potassium permanganate to remove traces of organic matter, and then reduced by a current of sulphur dioxide. After the expulsion of the excess of sulphur dioxide by boiling, the vanadyl sulphate which remains is estimated by titration at 70° C. with potassium permanganate solution. A repetition of the reduction and titration may be made with the same solution. The reaction may be expressed.

$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_5 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

Details are given of the conditions necessary for the satisfactory decomposition of various vanadium compounds by carbon tetrachloride. It is also possible to expel phosphoric acid from sodium phosphate by heating a mixture of the latter with sodium chloride or silica in carbon tetrachloride vapour ; boric acid and titanic acid can be displaced in a similar manner, but the details necessary to render the process capable of application to quantitative analysis are not yet worked out.

APPARATUS, ETC.

Inhibition of Foaming by Isoamyl Isovalerate. C. H. Fiske. (*J. Biol. Chem.*, 1918, **35**, 411-413; through *J. Soc. Chem. Ind.*, 1918, **37**, 606A.)—Isoamyl isovalerate is recommended as a foam inhibitor in analytical operations, and two methods are described for its preparation: (1) By heating a mixture of isoamyl alcohol and isovaleric acid in the presence of concentrated sulphuric acid, and (2) by oxidising isoamyl alcohol with potassium dichromate and sulphuric acid.

Substitutes for Platinum Electrodes in Electro-Analysis. P. Nicolardot and J. Boudet. (*Bull. Soc. Chim.*, 1918, [iv], **23**, 387-391.)—A discussion of the many proposals to use gold, gold-platinum alloys, copper, and certain proprietary iron alloys, is followed by a description of experimental work with gold-platinum alloys. For cathodes an alloy of gold and platinum in the ratio 7 : 1 serves well in all circumstances. The small variations in weight observed are no greater than those shown by platinum apparatus under similar conditions. As anodes such electrodes are less satisfactory, and must not be used for the anodic deposition of lead nor with cyanide electrolytes. If, however, they are electroplated with platinum (5 mgrms. per square cm.), they form quite satisfactory anodes. In ammoniacal solution such electrodes acquire a light brown colour and show an increase in weight of the order of 1 mgrm., but return to their original weight and appearance on heating to 300°C. As anodic depositions are not carried out in ammoniacal solutions, this property is a trifling inconvenience only, and not a source of error. G. C. J.

REVIEWS.

ANNUAL REPORTS OF SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. Vol. II., for 1917, Pp. 509 and Indexes. 1918. Price 4s. 6d.

The contributors to the second volume of the Annual Reports on the progress of applied chemistry published by the Society of Chemical Industry have well maintained the high standard reached in the first volume (see ANALYST, 1917, **42**, 318).

This volume of Reports, nominally for 1917, is much more extensive than the first one, as it deals with all the sections covered in the Society's Abstracts, with the exception of those on Explosives and the three Sections (Agricultural Chemistry, Chemistry of Foods, and Analysis) which are fully reviewed in the Annual Reports of the Chemical Society. The following twenty-one Sections are treated according to the individual standards of the authors, all experts in their particular branch:

Plant and Machinery (J. W. Hinchley);
Fuel (J. S. S. Brame);
Gas, Destructive Distillation, Tar Products (E. W. Smith);
Mineral Oil (W. J. A. Butterfield);
Colouring Matters and Dyes (G. T. Morgan)

Fibres, Textiles, Cellulose, and Paper (J. F. Briggs);
Bleaching, Dyeing, Printing, and Finishing (S. H. Higgins);
Acids, Alkalis, Salts, etc. (H. A. Auden);
Glass, Refractory Materials, Ceramics, and Building Materials (W. J. Rees);
Metallurgy of Iron and Steel (C. O. Bannister);
Metallurgy of the Non-Ferrous Metals (G. Patchin);
Electro-chemistry (A. J. Hale);
Oils, Fats, and Waxes (E. R. Bolton and C. Revis);
Paints, Pigments, Varnishes, and Resins (R.S. Morrell);
Indiarubber (H. P. Stevens);
Leather and Glue (J. T. Wood);
Sugars, Starches, and Gums (T. H. P. Heriot);
Fermentation Industries (A. R. Ling);
Water Purification and Sanitation (S. Rideal);
Fine Chemicals, Medicinal Substances, and Essential Oils (F. L. Pyman);
Photographic Materials and Processes (B. V. Storr).

These authors have in most cases contributed a critical and readable report on the progress of their own subject, having successfully avoided the compilation of a mere catalogue of papers, so that the few criticisms that occur to the reviewer are concerned with the work of the Publication Committee.

It is unfortunate that the present volume has no preface to explain what periods are covered by the Reports on the various Sections. Although all are nominally for the year 1917, some of these cover one, some two, and in other cases appear to cover even more than two years back. In future volumes it is very desirable that a list of the abbreviations used in the references should be given, and it is to be hoped that arrangements can be made that such abbreviations should be the same as those used in the Annual Reports issued by the Chemical Society.

The Reports are necessarily compiled quite independently by the various authors, but repetition should be avoided. Thus, there seems no reason, for example, for the descriptions of a patent by Röhm appearing in three different Sections; the mention of the "activated" sludge process of sewage purification in the Section on Leather and Glue, when it is properly and fully described in the Section on Sanitation; or for two references to a somewhat theoretical paper on the theory of azo dyestuffs: whilst the Section on Electro-Chemistry in several places duplicates matter found in other parts of the volume. Again, it is curious to find the detailed description of an important paper by Perkin on the Constitution of Cryptopine (the alkaloid occurring in very minute quantities in opium), as the same paper is described at length in the Annual Report of the Chemical Society for 1916. It is not easy to distinguish between what should be dealt with in a report on pure chemistry and that in a report on applied chemistry. It is, however, obvious that a considerable part of the work so ably treated in the present volume would not be out of place in the Annual Reports of the Chemical Society, whilst as a matter of fact several papers referred to in this volume are dealt with in the Chemical Society's Reports. This point naturally suggests further co-operation between the Chemical Society and the Society of Chemical Industry, and it should not be difficult for their Councils to

arrange that the Annual Reports on the progress of Pure and Applied Chemistry should be prepared by a Joint Publication Committee.

ROBERT H. PICKARD.

MONOGRAPHS ON INDUSTRIAL CHEMISTRY. THE APPLICATIONS OF ELECTROLYSIS IN CHEMICAL INDUSTRY. By A. J. HALE. Pp. 148. 1918. London: Longmans, Green and Co. Price 7s. 6d. net.

The chemical industries based on applied electrolysis are likely to be of great importance in the future, though as yet they are not developed to any considerable extent in this country. Partly as a consequence of this, the practical knowledge in this field of inquiry is not very widely disseminated, and there is therefore a need for a satisfactory monograph. Mr. Hale's book, which belongs to Sir Edward Thorpe's now well-known series, is an attempt to supply an account of the applications of electrolysis in chemical industry. It is written from the point of view of the beginner, and it is suitable, therefore, for third-year or evening-class students wishing to make a speciality of this branch of their subject. We fear it will prove a disappointment to those engaged in the practice of the industry, both because it lacks any real grip of the subject and is without imagination and stimulus. Considered, however, solely from the point of view of a student's text-book, the book is conscientiously done.

After introductory sections on electrolysis and methods of generating the current, the subjects dealt with in turn are the electrolytic refining and winning of metals, production of hydrogen and oxygen, electrolysis of alkali chlorides, production of inorganic and organic compounds by electrolysis. Ample note is taken of the patent literature, and there are numerous references to original papers.

E. F. ARMSTRONG.