THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

THE following candidates have been elected members of the Society:

Cyril Dickinson, B.Sc. (Vict. and Leeds), F.I.C., Public Analyst and Bacteriologist.

Arthur Geoffrey Grimwade, M.A. (Cantab.), A.I.C., Chemist in Government Department.

Ernest Avery Roff, B.Sc. (Lond.), Chief Analyst and Research Chemist with Chemical Manufacturers.

Samuel John Rowland, B.Sc., Ph.D. (Reading), A.I.C., Research and Analytical Chemist at Dairying Research Institute.

Franklin Clermont Scott, B.Sc. (Lond.), A.I.C., Analytical Chemist with Chemical Manufacturers.

Herbert Lawton Wright, Chief Chemist at Beet Sugar Factory.

Death

WE regret to record the death, on August 26th, of

Albert John Murphy,

who had been a member of the Society for forty years.

The Spectrographic Analysis of Tobacco Ash

BY F. G. H. TATE, F.I.C., AND H. KENNETH WHALLEY, B.A., B.Sc., PH.D.

ALTHOUGH much work has been devoted to the constituents of tobacco such as sugars, proteins, water, nicotine and total ash,[1] and to the influence of soil conditions upon the proportions of these constituents,[2] the systematic inorganic analysis of tobacco ash appears to have received little attention. Further, the determination of the area or country of origin of tobacco by chemical or other means has presented a problem for which no satisfactory solution has yet been found.

In the discussion of a paper,[3] and subsequently, one of us suggested that spectrographic methods of analysis might be of use in attempting the differentiation of sources of origin of tobacco. Following this suggestion, analyses have been made of over 300 samples of tobacco ash, involving more than 3000 quantitative

and partly quantitative determinations. Evidence has thereby been accumulated which not only supplies new data on tobacco constituents but also indicates the lines upon which discrimination between certain different types of tobacco can be made with a high probability of success. Preliminary work was carried out by arcing a 50/50 mixture of the ash with oxides of lead and tin, the spectrum lines of the lead and tin serving as internal standards with which lines due to the constituents of the ash were compared. By comparison of the spectra obtained with those of standard synthetic mixtures (*i.e* synthetic ash plus lead and tin oxides) rough estimates of the composition of a fair number of ashes—Empire and non-Empire, lamina and stalk, in all about 80 samples—were made. From this examination it appeared that certain chemical differences existed between different types of tobacco ash. As these differences appeared to be characteristic and not random, a detailed examination was made of a larger number of samples, as follows:

Light Virginian type from source A, lamina 26, stalk 23; from source B, lamina 22, stalk 10; from source C, lamina 50, stalk 40; from source D, lamina 13, stalk 13. *Indian type* from source E, lamina 22. *Turkish type* from source F, combined lamina and stalk 10; from source G, lamina 8, stalk 8. *Miscellaneous types* 16. Total 261 samples.

Experimental

Ashing the Tobacco.—The tobacco was burned at a low temperature and the ash was treated with ammonium carbonate, and re-heated. The resultant ash was finely ground. Early analyses showed that occasionally carbonation was incomplete; consequently the practice was adopted, and is followed in this paper, of giving the major metallic constituents of the ash not as percentages of metal, oxide, or carbonate on the ash, but as ratios one to another, *e.g.* Ca/K, Mg/K and Mg/Ca. In this way irregularities due to variations in the nature and amounts of the acid radicles present are avoided.

Determination of Ca, K, Mg, Sr and Mn in the Acid Extract by the Lundegardh Method.—An apparatus similar in its essential features to that described elsewhere[4] was constructed. The principle of the method is that the material to be examined is dissolved in some convenient liquid and the solution so obtained is atomised in the air supply of an air-acetylene flame. Conditions of the flame, *e.g.* air and acetylene pressures, are standardised and the spectra are photographed with a Hilger Medium Spectrograph, using Zenith plates. Actually 0·1 g. of the ash was treated with 10 ml. of water and 4·5 ml. of 4 *N* hydrochloric acid, allowed to stand on the steam-bath for ½ hr., boiled for 2 mins., diluted and filtered and the filtrate was made up to 100 ml. This solution gave spectra of suitable density for potassium, magnesium, strontium, and manganese determinations. For the determination of calcium a (1+10) dilution was made. Duplicate spectra (1 min. exposures) of 10 samples and 6 standard solutions were photographed on one plate. The blackening of the spectrum lines (due to Ca, K, Mg, Sr and Mn) and that of the spectrum background in the vicinity of the lines were measured, using, in the earlier part of the work, a microphotometer previously described,[5] and later a Hilger microphotometer. The measurements so obtained were treated in the usual way, *i.e.* the ratio:

$$\frac{\text{deflection for line}}{\text{deflection for background}}$$

was plotted against percentages of the element present in the six standards, and from the curve drawn through the seven points (six from the standards, the seventh point corresponding to zero percentage and ratio 1·0) the percentages of the element present in the 10 samples were read off. The amounts of calcium, potassium and magnesium were determined throughout in this way. The amounts of strontium and manganese, which were small, were only occasionally determined by measurement; usually the plate was examined visually and the percentages of these two elements were estimated. The errors of the Lundegardh method are usually less than ±5 per cent. of the amount of the material determined, their precise magnitude depending upon the element determined, its

environment and its absolute concentration in the solution aspirated into the air stream. With standard solutions for which the preliminary physical and chemical treatment was well controlled, this degree of precision was obtained. The errors of the complete routine procedure, *i.e.* extraction of 0·1 g. of ash, filtration, etc., followed by spraying, were not unexpectedly greater. The repeatability of the whole process was tested by making a number of repeat determinations after some weeks or months. Table I gives typical results:

TABLE I

Sample No.	K Per Cent.	Ca Per Cent.	Mg Per Cent.	Ca/K	Mg/K	Mg/Ca
62	22·3	10·2	3·5	0·46	0·16	0·34
	22·0	11·5	3·5	0·52	0·16	0·30
90	15·6	13·5	3·0	0·87	0·19	0·22
	18·5	15·0	3·0	0·81	0·16	0·20
160	15·2	18·5	3·5	1·22	0·23	0·19
	18·0	21·0	3·5	1·17	0·19	0·17
226	8·2	14·0	3·0	1·71	0·37	0·21
	8·8	15·9	3·0	1·89	0·34	0·19

Estimation of Na, Li, Al, Si, B, Pb and Ba by the Arc Method.—About 10 mg. of ash were placed on the lower, slightly hollowed cathode of a pair of copper electrodes and the arc (200 v.; 2 amps.; gap 4 mm.) was struck. Duplicate exposures, each of 2 mins., were photographed, with Ilford Special Rapid Panchromatic plates, the spectrograms obtained were compared visually with those of synthetic mixtures, and estimates of the amounts of the elements present were made. To avoid the implication of a degree of accuracy which does not exist, we have preferred not to give the amounts so estimated as percentages, but to distinguish, for each element, only four (or three) grades of quantity, designated by the bracketed numerals (1), (2), (3) and (4). The approximate percentages to which they correspond, for the various elements, are shown in Table II.

TABLE II

	Na	Li	Al	Si	B	Pb	Ba	Sr*	Mn*
(1)	<0·1	<0·005	<0·5	<5	<0·02	<0·03	<0·005	<0·1	<0·03
(2)	0·25	0·005	0·5	8	0·02	0·03	0·03	0·3	0·1
(3)	0·5	0·01	2·0	12	0·08	0·15	0·14	0·8	0·2
(4)	—	0·04	4·0	16	0·40	0·8			

* Sr and Mn were visually estimated from Lundegardh plates.

Results of high precision were not obtainable from this simple arc, but duplicates taken at different times on different plates never differed by more than one grade, *e.g.* (2) repeated as (3), or (4) repeated as (3), and usually differences were of nil or a half grade, *e.g.* (2) repeated as (2), or (3) repeated as (3)–(4). More precise procedures, involving the addition to the ash of a standard amount of some element which gives lines to serve as internal standards, do of course exist,* but for this exploratory work the gain in accuracy did not appear to be worth the additional labour and loss of speed that quantitative arc methods involve. It must be remembered that the probable errors of derived averages, distributions, and such values are very much less than the errors of the individual determinations.

To avoid systematic errors the samples were analysed in irregular order over a long period of time, and by three operators, one working over the whole period and two part time.

* See, for example, "*Spectrographic Analysis in Great Britain*," A. C. Candler (Adam Hilger, Ltd.), p. 47; "*Paints, Varnishes and Fabrics*," by War Department Chemist. This method is used by one of us for the general analysis of non-conducting powders.

Results

The *average* composition of the major groups of tobacco ashes examined are summarised in Table III.

Table III

Origin	No. of samples examined	Ca/K	Mg/K	Mg/Ca	Li	Al	B	Si	Mn	Na	Sr	Pb	Ba
A Lamina	26	0·90	0·15	0·16	(3)	(2)–(3)	(2)	(2)	(1)	(1)–(2)	(1)–(2)	(1)	(1)–(2)
B ,,	22	1·50	0·35	0·25	(2)	(2)	(2)	(2)	(1)	(1)	(2)	(1)	(1)–(2)
C ,,	50	1·58	0·23	0·15	(2)	(2)–(3)	(2)–(3)	(3)	(2)	(1)–(2)	(1)	(3)–(4)	(1)
D ,,	13	1·96	0·20	0·10	(1)	(2)	(2)–(3)	(1)	(2)	(1)–(2)	(1)	(3)–(4)	(1)
E ,,	22	2·88	0·58	0·20	(4)	(2)	(2)–(3)	(2)	(1)	(1)–(2)	(2)	(1)	(2)
F Lamina and stalk	10	3·64	0·39	0·11	(4)	(4)	(2)–(3)	(2)–(3)	(1)–(2)	(2)	(1)–(2)	(1)	(1)
G Lamina	8	1·72	0·49	0·33	(1)	(2)–(3)	(2)–(3)	(4)	(2)	(1)–(2)	(1)–(2)	(1)	(1)
A Stalk	23	0·36	0·11	0·33	(3)	(2)	(2)	(1)	(1)	(1)–(2)	(1)–(2)	(1)	(2)
B ,,	10	0·61	0·17	0·28	(2)	(2)	(2)	(1)	(1)	(1)	(2)	(1)	(2)–(3)
C ,,	40	0·58	0·12	0·21	(1)	(2)	(2)	(1)	(1)	(1)–(2)	(1)	(1)	(1)–(2)
D ,,	13	0·89	0·17	0·19	(1)	(2)	(2)	(1)	(1)	(1)	(1)	(1)–(2)	(1)–(2)
G ,,	8	0·96	0·36	0·39	(1)	(2)	(2)	(2)	(1)	(1)	(2)	(1)	(1)

Strong evidence that the differences revealed between the various ashes are real and not fortuitous is obtained from the "half-means," *i.e.* the averages of the first half and of the second half of the total number of samples examined. Table IV gives a number of these half-means for the ratio Ca/K.

Table IV

Tobacco	No. of samples	First half-mean	Second half-mean	Final average
C Lamina	50	1·68	1·47	1·58
C Stalk	40	0·57	0·59	0·58
H* Lamina	44	1·03	1·22	1·13
H* Stalk	35	0·39	0·45	0·42

* Includes A, B, and three miscellaneous samples.

It is interesting that though the values of Ca/K for the different types of lamina and stalk differ so markedly, the average value of the ratio, R, of Ca/K in stalk to Ca/K in lamina, for the five groups of tobacco ashes for which data are available, is relatively constant, as shown by Table V.

Table V

Tobacco	Number (n) of samples of (lamina and stalk)	$\Sigma R/n$
A Light Virginian Type ..	23	0·45
B ,, ,, ,, ..	10	0·41
C ,, ,, ,, ..	40	0·43 (Half-means 0·40, 0·45)
D ,, ,, ,, ..	13	0·45
G Turkish Type	8	0·62

These findings, taken in conjunction with Table III, reveal that for light Virginian-type tobacco: (1) the ash of the lamina and of the stalk show marked differences of average composition dependent upon the area of origin, *i.e.* upon *external* conditions such as soil, climate and cultivation; (2) though the average compositions of lamina and of stalk from different places differ, the average value of the ratio of Ca/K in stalk to Ca/K in lamina, which is governed by the *internal* balance and economy of the plant, appears to be substantially independent of external conditions, and approximately equal to 0·43.

Identification of Tobacco

Percentage Distribution Tables.—Table III shows that certain distinct differences exist between tobaccos from various areas, but *average* values would be of diagnostic use in only a small percentage of the cases encountered. To attempt identification or discrimination, the construction of distribution tables is essential. This has been done for A, B, C, and E laminae, and for A and C stalks, since data were derived from comparatively large numbers (22–50) of samples, and it is maintained that these may be used in processes of identification. Tables VI and VII, which are self explanatory, are typical percentage distribution tables.

Table VI. Distribution Table for Ca/K in Stalk

	Percentage of samples examined for which Ca/K falls within range:							
Source	0 to 0·20	0·21 to 0·40	0·41 to 0·60	0·61 to 0·80	0·81 to 1·00	1·01 to 1·20	1·21 to 1·40	1·41 to 1·60
A	4	61	26	9	0	0	0	0
C	2	23	23	33	10	7	0	2

Table VII. Distribution Table for Sr

		Percentage of samples with Sr contents:		
Source	Lamina or stalk	(1)	(2)	(3)
A	L	73	19	8
B	L	23	61	16
C	L	90	10	0
E	L	31	57	11
A	S	65	30	5
C	S	95	3	2

Diagnostic Use of Distribution Tables.—The diagnostic value of data of this type clearly depends upon whether the correlation and interdependence of the different characteristics are high or low. In the former circumstances the diagnostic value would be low; in the latter high. For example, the question may be put:—If a lamina ash from source C were to have a low Ca/K value which would tend to put it in the A group, would it also be likely to have other A characteristics (such as high Sr, Ba, Li, and low Pb, Mn, Si) or would the other properties be unassociated with the Ca/K value, so that a fair probability would exist of their values restoring the balance and bringing the sample back into its true group? No doubt this question could be answered by a statistical search for, and analysis of, the degree of correlation between the various characteristics. The alternative method, an outline of which is given below, is to attempt to determine the country of origin of a tobacco by means of the chemical analysis of the ash and the distribution tables given.

Ten ashes of tobacco from source A (both of lamina and of stalk), 10 from source C (both of lamina and of stalk) and 10 from source B (lamina only) were chosen as fairly as possible from the numbers previously examined; for example, every fourth sample of C source tobacco was chosen, and the B source laminas selected were those for which, by chance, the stalk ash had also been analysed. The problem set was to allot each of the 30 laminas to one of the three groups A, B, or C, and each of the 20 stalks into either the A or C group. This test appeared to be a fair one, since it was the sort of problem likely to be met in practice, and the characteristics of the 3 groups (see Table III) are not so widely different as those of some groups which might have been chosen, *e.g.* A and E.

From the distribution tables, probability factors may be derived. Consider, for example, strontium in the lamina ash. From Table VI we have

	Percentage with Sr contents:			
Source	(1)	(2)	(3)	Totals
A	73	19	8	100
B	23	61	16	100
C	90	10	0	100
Totals	186	90	24	

Hence probability factors are:

Source	Sr (1)	Sr (2)	Sr (3)
A	73/186 = 0·39	19/90 = 0·21	8/24 = 0·33
B	23/186 = 0·12	61/90 = 0·68	16/24 = 0·67
C	90/186 = 0·48	10/90 = 0·11	—
	0·99	1·00	1·00

Thus if a sample of lamina ash is found to contain strontium of amount (2), this indicates that the sample is most probably from B (probability factor 0·68), less probably from A (factor 0·21), and least probably from C (factor 0·11). Ideally, smooth distribution curves would be drawn from the distribution table data, and ideal, instead of actual, percentages read off from these curves and used for deriving probability factors; but the number of samples examined is not sufficiently large to allow the precise form of the distribution curve to be fairly drawn. Consequently it has been preferred to deduce probability factors from the percentage distributions which were actually determined by the examination of, say, N samples, rather than from percentages estimated for $N \to \infty$. In all, probability factors were derived in this way for Ca/K, Mg/K, Mg/Ca, Sr, Ba, Pb, Mn, Li and Si for laminas, and for Ca/K, Mg/K, Mg/Ca, Sr, Ba, Li for stalks, these being the characteristics which showed the greatest variations dependent upon area of origin.

The probability factors for each of the 50 samples chosen were assessed and their average values were taken. Below are given two typical examples.

	Sample of lamina from source C				Sample of stalk from source C			
		Probability factors				Probability factors		
Analysis		C	B	A	Analysis		C	A
Ca/K	1·32	0·23	0·58	0·19	Ca/K	0·48	0·47	0·53
Mg/K	0·14	0·43	0·14	0·43	Mg/K	0·04	0·49	0·51
Mg/Ca	0·11	0·37	0·17	0·46	Mg/Ca	0·09	1·00	—
Sr	(1)	0·48	0·12	0·39	Sr	(1)	0·58	0·52
Pb	(4)	1·00	—	—	Ba	(1)	0·61	0·39
Ba	(1)	0·34	0·31	0·35	Li	(1)	0·68	0·32
Mn	(2)	0·61	0·03	0·36				
Li	(2)	0·36	0·32	0·32				
Si	(2)	0·22	0·46	0·32				
Average probability factors		—	—	—	Average probability factors		0·64	0·36
		0·45	0·24	0·31				

It will be observed that in both instances the samples are correctly identified as from source C.

The outcome of applying this method to the 50 samples was:

Number of samples	Type	Correctly identified
10	A Lamina	9
10	A Stalk	8
10	C Lamina	7
10	C Stalk	10
10	B Lamina	9
Totals 50		43

An earlier attempt at identification, in which the probability factors for the characteristics Mg/K and Mg/Ca were not included, gave 40 correct out of 50. It appears possible, therefore, that if all the characteristics were to be included the probability of a correct identification being made would increase. Such a comprehensive assessment, using all the data available, was not thought to be worth the additional labour involved, since already the desired principle had been demonstrated, namely, that a method of identification with a high probability of success, of the place of origin of a tobacco, may be based upon the analysis of its ash.

The method would be improved by the use of more precise methods of analysis, particularly in the arc technique, and by the accumulation of more data. As a standard procedure for indicating the source of an unidentified sample it may be necessary to add at intervals to the collected data those for new known samples from current production, at the same time removing from use the data for an equal number of the earliest samples. This would accommodate the method to any gradual changes which may be in progress.

Though 43 out of the 50 samples chosen were correctly identified, it should be remembered that by tossing a coin or spinning a roulette wheel the chances are that the correct answer would have been made in $\frac{30}{3} + \frac{20}{2} = 20$ cases out of the 50 chosen.

SUMMARY.—Analyses have been made of over 300 samples of tobacco ash. New data have been obtained on the inorganic constituents and on their dependence or otherwise upon the area of origin. The *average* composition of the ashes of tobaccos from certain different areas showed distinct differences. From a statistical treatment of the results, probability factors were derived which had high diagnostic value. It is demonstrated that a method of identifying the source of tobacco, with a high probability of success, may be based on analysis of the ash.

We are indebted to Drs. McClelland and Fay who at different times helped with the experimental work, and to Mr. G. H. Dyer for practical assistance throughout.

We thank the Government Chemist, Dr. J. J. Fox, C.B., O.B.E., for his permission to publish this account.

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September, 1940

The Analytical Constants of Spirit Vinegar

By C. H. MANLEY, M.A., F.I.C.

Recent experience has indicated that appreciably lower figures must be accepted for the minimum percentages of ash, nitrogen and phosphoric oxide in spirit vinegar than those put forward by Edwards and Nanji[1] in their valuable paper on the oxidation, iodine and ester values of vinegars. Also, under certain conditions, the oxidation value, but not the iodine value, may come within the malt vinegar range.

As a sequel to the mislabelling of bottles of spirit vinegar on sale in the Leeds area as "Genuine Vinegar (Non-Synthetic)," visits were paid to the wholesalers and to the manufacturers' distributing centre, it being considered that a product described as above should be malt vinegar. It was then learnt that the manufacturers were supplying a spirit vinegar concentrate containing approximately 12 per cent. of acetic acid to the wholesalers, who were then diluting it with water to three volumes prior to distribution to local shopkeepers, including fish and chip friers. The manufacturers also, when required, were themselves prepared to supply the diluted article, which was then quite properly labelled "Spirit Vinegar" in bold type.

The wholesalers subsequently agreed to label their product in similar manner as "Genuine Spirit Vinegar" and to omit the words "Non-Synthetic," previously printed in very small type.

The following table gives the percentage (g. per 100 ml.) results of the analysis of various samples obtained direct both from the manufacturers and from the wholesalers. The products supplied by the manufacturers may be accepted as genuine spirit vinegar.

Table I

Source	Acetic acid	Total solids	Ash	Nitrogen	P_2O_5	Oxid. value	Iodine value
1. Manufacturers' concentrate	11·94	0·17	0·032	0·003	0·005	464	30
2. Wholesalers' concentrate	11·80	0·55	0·044	0·016	0·005	272	38
3. Manufacturers' spirit vinegar	4·14	0·20	0·024	0·006	0·003	142	21
4. Wholesalers' spirit vinegar (A)	3·92	0·43	0·044	0·007	0·004	1120	46
5. Do. (B)	3·90	0·26	0·028	0·006	0·002	211	14
6. Do. (C)	4·12	0·20	0·018	0·011	0·003	109	13
7. Do. (D)	4·27	0·19	0·016	0·005	0·003	159	18
8. Water from rinsed cask before making (C)	—	—	—	—	—	3	4
Spirit vinegar, normal range	—	0·16–0·30	0·016–0·090	0·005–0·040	0·002–0·03	—	—
Do. (Edwards and Nanji)	—	0·16–0·30	0·04–0·09	0·03–0·04	0·002–0·03	88–225	8–27
Artificial vinegar, normal range	—	0·1–0·5	0·005–0·05	nil–0·04	nil–0·03	1–16	2–252
Do. (Edwards and Nanji)	—	0·30–0·45	0·02–0·05	do.	do.	do.	do.

Apart from the ash of No. 4 (the somewhat exceptional character of which is discussed below), all the samples of spirit vinegar examined had values for ash, nitrogen and phosphoric oxide well below the minima cited by Edwards and Nanji.

But for their oxidation values these vinegars would ordinarily be classified as artificial. The nett effect, therefore, is to render any determinations other than that of the oxidation value of very little use in distinguishing between artificial and spirit vinegars.

It will be seen that, whilst the oxidation value of No. 3 is less than one-third of that of No. 1, the oxidation value of No. 4 is more than four times that of No. 2, the concentrate from which it was prepared, the value in fact being equal to that of a malt vinegar. It transpired that these particular wholesalers make a practice of diluting their concentrate in 60-gallon Australian white wine casks, and that the sample in question represented a mix made in a fresh cask, from the walls of which the spirit vinegar had evidently extracted much of the residual alcohol. Thus pronounced odours of acetaldehyde and iodoform developed during the determinations of the oxidation and iodine values respectively. A sample (No. 5) taken from the second mix in the new cask gave an oxidation value (211) falling within the spirit vinegar range, but actually not much lower than that of the original concentrate. A further fall (to 109) occurred in the third mix (No. 6) made in my presence after the cask had first been washed out by filling with water (No. 8) and emptying. A sample of this water gave very low oxidation and iodine values. On my advice, 20 gallons of this concentrate were mixed with 38 gallons of water instead of with 40 gallons as hitherto, in order that the percentage of acetic acid in the spirit vinegar might not be less than 4 per cent. A further sample (No. 7) bottled off two months later from a subsequent mix made in the same cask showed, contrary to expectation, a rise in the oxidation value to 159, instead of a further fall to a figure between 90 and 100.

Determinations of the iodine value and of the percentage amounts of the chemical constituents, as well as the appearance of the total solids (whether mottled or not) would readily indicate whether a sample with an abnormally high oxidation value were a malt vinegar or otherwise.

The ester values of five of the seven samples of spirit vinegar were determined, and the following results (corrected for a 4 per cent. acid content) were obtained:

TABLE II

No.	Ester value	Ester value corr. for 4% Acetic acid
1	24·2	8·1
2	17·3	5·9
4	3·6	3·7
6	5·3	5·1
7	4·8	4·5 (duplicate sample kept 4 months)
Normal figures	6·0–14·0	
Do. after 18 months' storage	2·0–3·6	

The fixed acidity of No. 4 was only 0·002 per cent. (as tartaric acid), so that it would seem to be impracticable to separate any tartrate extracted from the wine cask. This would apply still more to the three subsequent mixes (Nos. 5, 6 and 7).

It is obvious that the ester values will not afford much help with the problem, although they show a slight decrease after the vinegars have been kept for nine months. The determination of the oxidation value, however, still remains the most sensitive test for distinguishing between spirit and artificial vinegars.

On the other hand, it would appear possible to pass off artificial vinegar as spirit vinegar by diluting coloured strong acetic acid in a wine cask, provided that the operation were not repeated more than once.

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Notes

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

DETECTION OF BEEF FAT IN LARD (BÖMER NUMBER)

A NEW modification of this method, proposed by an American Chemical Society Committee, has recently appeared (Abst., ANALYST, 1940, **65**, 508), but the full description is not sufficiently detailed to ensure satisfactory deductions from the results it yields.

Attention may be drawn, first, to the following point. It is directed that 20 g. of lard are to be treated with acetone at 30° C. and the solution diluted to 100 ml. with acetone at 30° C. It is evidently intended that solution should be complete and the liquid clear at this point.

The solution is then kept at 30° C. for 18 hours. Crystals are frequently deposited during this period, but I have encountered a large number of samples in which no crystals formed, and in some of these the lard was known to contain beef fat in admixture. Since absence of crystals is taken at present to indicate absence of hard fat, it follows that some adulterated lards may be classed as pure with the test in its present form. The difficulty originates in the abnormal stability of some supercooled lard solutions, and may be simply overcome by making a clear solution of the lard as directed, cooling it until crystallisation has started, and then placing it in the constant-temperature bath at 30° C. for 18 hours. Variations in the speed with which the initial crystallisation is allowed to take place do not affect the m.p. of the glycerides or fatty acids, and it makes no difference whether cooling is allowed to proceed until a heavy deposit has formed or is checked while the deposit is still small. Similar difficulties arise with regard to the induction of crystallisation in the corresponding B.P. test in which ether is used as solvent.

Secondly, a temperature variation of 4 degrees is allowed in both the A.C.S. method and the B.P. method during the standing period. Crystals may often be obtained at the lowest permitted temperature but not at the highest. If such crystals are of low melting-point, as may happen, conflicting deductions can be drawn from the results of either method. Such conflict would be avoided if temperature variations permissible were reduced to a fraction of a degree. It is a simple matter to maintain the fat solution within ±0° C. of a mean temperature in a constant-temperature bath, and mean temperatures of 30° C. (A.C.S. method) and 18° C. (B.P. method) are suggested as most satisfactory.

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October 9th, 1940

SAMPLING OF PRINTED PAPER

ON several occasions, in circumstances in which sampling has been difficult, these laboratories have had to determine poisonous metals in a sheet of printed paper to be used for wrapping foodstuffs. Unless the printed design is symmetrical, the sheet cannot be sampled by cutting out a portion of it, for there may be as many as eight or ten printings, each with a different ink, any of which may be responsible for the poisonous metal-content of the sheet. Destroying the whole of such a sheet by wet oxidation and taking an aliquot part of the resulting solution is one way out of the difficulty, but wet oxidation is inconvenient if the sheet is large and, further, if the whole sheet is used at once, there is no opportunity for replicate determinations unless more sheets are available. Even then, one cannot be certain that all sheets will carry the same amount of ink, as the thickness of the ink film printed may vary during a printing run. The need of some method of dividing a single sheet of printed matter to obtain a representative sample will therefore be apparent. A method of sampling which has been found to give satisfactory results is as follows:

The whole of the sheet is cut up into small pieces, about 2 or 3 mm. square. This is the most tedious part of the operation and is best carried out by first cutting the sheet into strips on a guillotine and then cutting the strips across. The pieces are then mixed by an air blast in a Buchner flask fitted with a cork and a lead-in tube for the air reaching to the bottom of the flask. About two or three minutes' mixing, while the flask is shaken at the same time to break up drifts, will generally be sufficient. Obviously care must be taken not to have the air blast so strong that the paper is blown out of the side tube of the flask and, in addition, the air should not be either very dry or very wet, otherwise the moisture-content of the paper may be altered. After mixing, the paper pieces can be turned out of the flask and quartered in the usual manner until a sample of convenient size is obtained.

The method was tested by taking known weights of four differently coloured papers, cutting them up, mixing in the manner described, quartering, and analysing the sample thus obtained by hand-picking to determine the proportion of each colour present. The results obtained showed a sampling error of about ±6 per cent, the extremes being +6·6 per cent. and −6·5 per cent. A typical series of results is as follows:

Substance of paper, 52 g. per sq. metre; size of pieces, 2 to 3 mm. square; number of quarterings, 2.

Paper	Wt. taken g.	Wt. found in quartered sample g.	Per cent. wt. found / Per cent. wt. taken	Deviation from mean Per Cent.
Blue	0·629	0·163	25·9	+4·0
Orange ..	0·613	0·144	23·5	−5·6
Yellow ..	0·508	0·123	24·2	−2·8
Pink	0·609	0·158	25·9	+4·0
Total ..	2·359	0·588	Mean 24·9	

The error involved is probably larger than the experimental error in some analytical determinations which would be carried out on the sample thus obtained, but for many purposes, *e.g.* determining whether the sheet complies with a specified limit for lead or arsenic, the accuracy is sufficient.

An attempt to reduce the sampling error by cutting the sheet into smaller pieces, 1 mm. square, gave no improvement in accuracy and the cutting up process then became impossibly tedious for any ordinary purpose. This drawback might be overcome by grinding the paper if a suitable machine were available. The method was tested on light-weight papers (52 g. per sq.m.) and heavier papers (460 g. per sq.m.), and a similar degree of accuracy was obtained in every instance.

I wish to thank the Council of the Printing and Allied Trades Research Association for permission to publish these results.

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August, 1940

Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1939

"CHEESE SPREADS."—Three samples bore an unsatisfactory label on which the fat contents were stated to be "25 per cent. i.d.s." as a minimum. The three letters were intended to mean "in dry solids," but the ordinary purchaser would be apt to imagine that the actual amount of fat present was 25 per cent., whereas only 12·7, 14·0 and 15·5 per cent. respectively were present, and in each instance the proportion of water exceeded 60 per cent. If it was intended that the amount of fat should be calculated as percentages of the dry solids of the cheese, this should have been stated on the label in plain terms and not in unintelligible abbreviations.

RASPBERRY JAM.—A sample of lower fruit standard raspberry jam was reported as deficient of 34 per cent. of fruit. The manufacturers contended that the correct amount (20 per cent. of the total bulk) was present, and they accounted for the low insoluble solids in the jam by alleging that the variety of raspberries used was liable at times to give an abnormally low figure for these constituents. Such abnormality, however, has only been detected in fruit grown in a particular district in Scotland and picked in late summer.

SODAMINT TABLETS.—Several samples did not agree in composition with formulae in the B.P. Codex. Three samples contained only a trace of ammonium bicarbonate and two contained none at all. The vendors of these were cautioned.

FORMALIN TABLETS.—The B.P. Codex requires each tablet to contain 9·7 mg. of paraformaldehyde. Whilst some samples complied with this formula, several others did not. One sample consisted of three varieties of tablets containing from 0 to 4 mg., of paraformaldehyde, another contained only 4 mg., and a third only 2 mg. The vendors were cautioned. As the names sodamint and formalin tablets are given as synonyms for the official Latin names in the Codex, it would prevent confusion if manufacturers would adhere strictly to the formulae and if other names were given to tablets not made according to the Codex prescription. It is unfortunate, to say the least, that a purchaser may get any one of several different articles all sold under the same description.

H. H. BAGNALL

Department of Scientific and Industrial Research

REPORT OF THE BUILDING RESEARCH BOARD FOR THE YEAR 1939*

DESCRIBING the functions of the Research Station in war time the Chairman of the Board (Mr. G. Mowlem Burt) mentions that it is (1) supplying data relative to a particular problem, (2) investigating new materials and methods of construction, and (3) investigating the use of alternative materials. The Director (Dr. Stradling) was asked during the year to undertake the duties of Chief Adviser on Research and Experiment to the A.R.P. Department.

In his Report on General Research and Investigation the Director gives an outline of further work on various problems.

CLEANING OF BUILDINGS.—The method of continuous spraying has been successfully applied to more buildings, including parts of Trinity College and other Cambridge colleges. It has also been successfully used on concrete buildings in London. The stains that developed on the Admiralty Screen, Whitehall, after it had been cleaned have faded appreciably during the year.

EFFECT OF LIME IN FIRED CLAY PRODUCTS.—The defect known as "lime-blowing" is caused by the expansion of nodules of lime or calcium sulphate as they become hydrated. It is usually prevented by grinding the clay very finely or by "docking," *i.e.* soaking the bricks or tiles in water when they are taken from the kiln. Local conditions must determine which method is the more suitable. In one works, "lime-blowing" could not be induced even by prolonged steaming of bricks after the method of fine grinding had been adopted.

SAND-LIME BRICKS.—It has been found that the properties of the bricks are considerably affected by the state of the silicate bonding material formed during the autoclave process. The silicate may be either wholly crystalline or entirely amorphous. A study of the factors influencing crystallisation should make it possible to control more closely the properties of those bricks.

PROPERTIES OF POROUS BODIES.—This investigation has proceeded along three main lines:

(1) *Crystallisation of Salts within the Pores.*—The "crystalline test" (in which the material is immersed in sodium sulphate solution and then dried to induce crystallisation in the pores, the process being repeated several times) has enabled the weathering qualities of natural building stones to be assessed and has provided a means of distinguishing good limestones or bricks from those of inferior quality.

(*a*) *Effect of the Temperature of the Sodium Sulphate Solution.*—It has been found that at temperatures above 30° C. no disintegration of natural stones occurs in the crystallisation test. This is due to the fact that 30° C. is higher than the transition temperature of sodium sulphate decahydrate, the formation of which within the pores can set up stresses greater than the tensile strength of natural stones.

(*b*) *Rate of Accumulation of Salt in the Pores.*—When samples of the stones were tested with the sodium sulphate solution above 30° C. there was for each specimen an initial increase in the salt content, but finally a limiting constant value was reached.

(*c*) *Diffusion of Salt from the Stone.*—When a specimen of stone containing salt was placed in water, the rate of diffusion of the salt varied not only with its concentration, but also with the type of stone.

(2) *Relation between Frost-resistance and Pore Structure.*—An apparatus has been devised for measuring the changes in linear dimensions of a material when the crystals are formed within the pores. It has been found that the formation of ice within the pores of clay bricks results in an increase in linear dimensions. The nature of the change varies with the type of brick.

ARTIFICIAL WEATHERING OF ASPHALT.—By removing the normal surface finish obtained by sanding the ultimate degree of whiteness was more rapidly obtained. The removal of the surface was effected by cutting and grinding with carborundum.

FINENESS OF PORTLAND CEMENTS.—An air permeability method for measuring the surface area of cements has been found to afford a rapid means of estimating the specific surface of fine powders (*cf.* Lea and Nurse, *J. Soc. Chem. Ind.*, 1939, **58**, 278).

RESISTANCE OF CONCRETE AND MORTAR TO ATTACK BY CHEMICAL AGENTS.—Waste waters from the milk industry were found to cause softening of Portland cement mortars, whereas high alumina cement was entirely unaffected (Lea and Bessey, *Concr. Constr. Eng.*, 1939, **34**, 610).

"CRAZING" OF CAST CONCRETE PRODUCTS.—A quick laboratory method of testing the liability of cast concrete to "craze" has been devised, the samples being alternately wetted and dried in a cycle of treatments under standard conditions; it has given promising results.

UTILISATION OF BLAST FURNACE SLAG.—Slag has been used for many purposes as an aggregate of concrete. The only trouble so far reported appears to be due to the presence of small amounts of sulphate producing expansion in the concrete. A maximum of 0·5 per cent. of sulphate, expressed as SO_3, in the aggregate of sand size is apparently a safe permissible limit.

PATTERN-STAINING OF CEILINGS.—Aitken's investigations (*Proc. Roy. Soc. Edinb.*, 1884, **12**, 440) proved that dust tends to move from hot surfaces and to attach itself to cold ones. They

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* H.M. Stationery Office, York House, Kingsway, London, W.C.2. Price 1s. net.

afford a satisfactory explanation of the stains on plaster ceilings, in which the pattern of the construction behind the plaster is revealed. Experiments described dispose of the fallacy that the patterns are due to dust passing through the plaster. Recently there have been numerous instances of pattern-staining on hollow-tile ceilings. To prevent this, sufficient thermal insulation must be provided to reduce the heat flow through them to the level of the flow through the hollow tiles.

THE TESTING OF AIR FILTERS.—Two sets of apparatus for testing the efficiency of air filters have been devised. One of these is portable and is primarily designed for filters in commercial use; the other is a laboratory plant capable of accommodating single filter-units, which are usually 20 in. square.

New South Wales

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1937

THE Government Analyst (Mr. S. G. Walton) reports that 34,569 samples were examined under the Pure Food Act and 2292 for the Public Services. The food samples consisted principally of milk (25,903), and of these, 369 were adulterated. Among the points of interest discussed in the Report are the following:

BREAD STANDARDISATION.—Representations were made by an Inter-State Nutritional Advisory Board, to investigate the possibility of producing an absolutely standard white flour for bread. It was found that in New South Wales the nitrogenous content of wheat materially increased from the south to the north; hence the production of an absolutely uniform bread appeared impracticable, although the amended standards for wheatmeal, wholemeal and brown bread provide for products of approximately uniform composition. It might be advisable, however, to increase the prescribed minimum nitrogen-content of flour from the present figure of 1·2 per cent.

SULPHUR DIOXIDE IN BEER.—The Regulations allow preservative to be added to bulk beer (if declared), but not to bottled beer or stout. Since traces of sulphur dioxide will generally be found in beers, it is recommended that the presence of total sulphur dioxide in the proportion of not more than 1 grain per gallon should be permitted without declaration; when the amount exceeds that proportion, its presence should be declared on the container.

VEHICLE FOR ESSENCES.—The Regulation permits the use of ethyl alcohol or some other harmless vehicle for essences. A firm asked that consideration should be given to the use of propylene glycol for this purpose, and sent an account of experiments that had been made. It was found, however, that this work had been restricted to one isomer only ($CH_3.CHOH.CH_2OH$), and was chiefly concerned with the effect on rats of drinking considerable amounts of that liquid. Propylene glycol is not recognised by the B.P. or B.P.C. for pharmaceutical purposes, and it was decided that, unless there was evidence that it is not more toxic than ethyl alcohol, its use could not be permitted.

GELATINOUS PROTECTIVE COATING FOR FOOD STUFFS.—An application was made for permission to use a gelatin compound hardened with formalin as a protective coating for hams, etc.; it was claimed that the formaldehyde did not penetrate into the meat, and, as the coating would be removed before cooking or eating, no harm could result to the consumers. On investigation it was found that the formaldehyde did penetrate into the meat, and the application was refused. Subsequently an application was received from another firm who wished to use a coating of gelatin hardened with potassium dichromate for the same purpose. In view of the previous experiments, it seemed probable that small amounts of chromium would penetrate into the meat, and, since the addition of chromium compounds to foodstuffs is prohibited under the Pure Food Act, this application was also refused.

ADDITION OF STABILISER TO MILK BEVERAGES.—Application was made for permission to add a stabiliser to chocolated or malted milk sold in bottled form. The stabiliser suggested (sodium alginate) may be regarded as harmless, but the danger of permitting its use is in the creation of a precedent for using this and other substances (gum, gelatin, viscogen, etc.) in cordials, creams, etc., in which its presence may mislead the purchaser into thinking that the thicker the article the better the quality. It was recommended that this aspect of the question should be taken into consideration, and that if the application were granted, a standard should be framed prescribing a minimum milk-content, since such a beverage would enter into competition with fresh milk shakes, etc.

MOULD-CONTENT OF TOMATO PRODUCTS.—A Regulation has been made providing that the mould-content of tomato sauce or purée shall not exceed 50 per cent. of the microscopic fields examined, as determined by the method of the Association of Official Agricultural Chemists, U.S.A. It was proved that the mould-content of tomato pulp depends not so much on the variety of tomatoes as on the efficiency of sorting and trimming.

CARBOXIDE AS A FUMIGANT FOR FOODSTUFFS.—Carboxide is a mixture of ethylene oxide (about 1 part) with carbon dioxide (about 8 parts). The U.S.A. Dept. of Agriculture found that ethylene oxide was highly toxic to insects infesting food products, and no deleterious effects were

noticeable on foods such as dried fruits after exposure for 24 hours to the fumigant. Later it was found that a mixture of 1 vol. of ethylene oxide with 7·15 vols. of carbon dioxide was normally non-inflammable and materially increased the toxicity of the fumigant to insect life. It would appear from these experiments that carboxide may safely be used for exterminating insect pests in stored foods.

CAMPHORATED OIL.—Two samples were condemned—one because it had been prepared with maize oil and the other because soya bean oil had been used.

PERCAINE AND PROCAINE.—A medical practitioner prescribed a 0·2 per cent. solution of novocaine in normal saline as a local anaesthetic during an operation. During the operation the patient died, and, as his general condition did not appear to explain the collapse, a death certificate was refused. It was found after the post-mortem and chemical examinations that percaine was present in the organs and that percaine had been substituted for novocaine by the dispenser in making up the prescription. At the Coroner's inquest the evidence showed that the dispenser was under the impression that percaine and novocaine (procaine) are synonymous, and that he was not aware that the former is ten times as toxic as the latter. Unfortunately there are a number of drugs with closely similar names or synonyms, the toxicity of which varies widely. While this is so, accidents of this nature are likely to recur.

Another death from this drug occurred through a patient swallowing some of the percaine used as a local anaesthetic during an operation on the throat.

PASTEURISATION OF CREAM BY THE "FLASH" PROCESS.—As it was suspected that certain cream was not being heated to the stipulated temperature of 178° F. in accordance with the requirements of the Pure Food Act, an investigation was made to ascertain if the chemical tests applied could be relied upon for Court purposes as giving accurate results with regard to the heat treatment of cream. In the experiments, described in detail, the Storch peroxidase test and Kay and Graham's phosphatase test were used. The samples of milk and cream were collected in duplicate, so that a series of tests could be made as soon as possible after collection, and then another series of tests made on the following day, the samples meanwhile being kept on ice. So far as could be ascertained, no alteration took place in the enzymes of the cream, and therefore examination 24 hours after the samples have been collected and kept under proper conditions may be regarded as a reliable guide to the presence, or otherwise, of the enzymes in question. The experiments indicated that the cream under examination had been inadequately pasteurised. No subsequent trouble was experienced, the samples examined conforming with the results of the investigation.

DETERMINATION OF ALCOHOL IN PRESENCE OF ACETONE IN DISTILLATES FROM BLOOD OR URINE.—A method devised by the Government Analyst and R. G. O'Brien has been modified for use in presence of acetone. Denigès found (*J. Pharm. Chim.*, 1899, **9**, 7; Abst., ANALYST, 1899, **24**, 92) that when acetone is boiled with mercuric sulphate and sulphuric acid it forms a crystalline complex, and in the authors' experience this test is sufficiently accurate to detect and determine less than 1 mg. of acetone in presence of considerable quantities of alcohol. A suitable quantity of the distillate (obtained with a simple apparatus previously described), ranging from 1 ml. to 10 ml. according to the alcoholic content, is diluted to 40 ml. with water, and added to a cooled mixture of 15 ml. of $N/5$ potassium dichromate solution and 20 ml. of conc. sulphuric acid (sp.gr. 1·83) contained in a 100-ml. acetylisation flask (fitted with a ground-glass condensation tube, 1 m. long and approx. 1 cm. in diameter). The flask is immersed in water at 78° to 80° C. for 30 minutes, after which its contents are transferred to a 600-ml. flask, the acetylisation flask being rinsed with 2 portions of water (100 ml. each) and then with 25 ml. of water, and the washings added to the main solution. The flask is rapidly cooled to room temperature, and its contents are made up to about 500 ml. About 1 g. of potassium iodide is added, and the liberated iodine is titrated with $N/10$ sodium thiosulphate solution. A blank determination is made to obtain the corrected amount (n) of thiosulphate consumed. The mg. of alcohol in the distillate used $= n$ ml. of thiosulphate $\times$ 1·15 $- y$, where y represents the correction to be applied in presence of acetone as determined by the Denigès method. For each mg. of acetone present 0·029 mg. of absolute alcohol is deducted from the amount found. It is unlikely that in this method a correction of more than 1 mg. of alcohol will ever have to be made.

United Provinces and Central Provinces, India

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR 1939

THIS is the 75th Annual Report of the Department, which is under the control of Dr. S. N. Chakravarti, F.I.C. During the year under review 3481 cases were investigated as compared with 3185 in 1938. In the medico-legal section 1615 cases were dealt with as against 1524 in 1938.

HUMAN POISONING.—The total number of cases examined was 413, and poison was detected in 60·5 per cent. Of the detected poisons, datura headed the list (37·5 per cent.), followed by opium (23·5 per cent.), arsenic (18·6 per cent.), mercury salts (3·7 per cent.), aconite (3·0 per cent.), cyanides (2·3 per cent.), nux vomica (1·9 per cent.), and alcohol (1·1 per cent.). Other organic poisons found included *Abrus precatorius*, *Lachitra*, yellow oleander, pink oleander and two unidentified vegetable poisons, and among the inorganic poisons were sulphuric and nitric acids and copper sulphate.

ANIMAL POISONING.—There were 36 cases as compared with 23 for the preceding year, and poison was detected in 66·6 per cent. Arsenic was detected in 14 of these cases and kaner (yellow oleander) in 2. There was one unidentified poison.

CREMATION REMAINS.—In cases of alleged poisoning the bones and ashes of five persons were examined, and arsenic was found in four of them.

Government of Madras

ANNUAL REPORT OF THE GOVERNMENT ANALYST TO SEPTEMBER 30TH, 1939

THE Government Analyst (Mr. H. Hawley, M.Sc., F.I.C.) reports that 8833 samples were taken under the Prevention of Adulteration Act (including 1326 examined by the Madras City Analyst). These comprised 2310 of ghee (837 adulterated), 3834 of milk (1878 adulterated), 334 of butter (87 adulterated), 1643 of gingelly oil (237 adulterated), and 712 of other foods (127 adulterated). The total percentage of adulterated samples was 35·8.

ADULTERATION IN MADRAS.—Adulteration in the Province continues to be practised on the grand scale. In some of the panchayats to which the Act has recently been extended more adulterated than genuine food is sold (*e.g.* in Madanapalle, 75 per cent. adulterated; in Mettupalaiyam, 73 per cent. adulterated). The fact that there is little or no improvement in those areas where the Act has been in force for a number of years appears to be due to the unwillingness of magistrates to impose really deterrent fines. The average fine for the whole Province is only Rs.27, and there are only two areas where it exceeds Rs.50. A fine of Rs.50 at infrequent intervals will not deter even the meanest hawker from foregoing the steady profits that he makes by selling food heavily adulterated with water or a cheap substitute for the genuine article. In General Order No. 346, Public Health, January 29th, 1938, the attention of magistrates was called to the large profits made by food adulteration and to the need for deterrent fines; but the Order appears to have had little or no effect. Another very disturbing fact is that in 9 cases, in which moderate fines of Rs.100 or less have been imposed by the magistrates, these have been reduced on appeal. If the imposition of heavy fines on small vendors is impracticable, it would seem that the Act should provide for imprisonment without the option of a fine when the adulteration is heavy and deliberate.

FREEZING-POINT OF MILK.—The Act prescribes a minimum limit of 9 per cent. of solids-not-fat in buffalo milk, but commonly the figure is 10 per cent., so that such a sample may contain 10 per cent. of added water. All samples showing 10 per cent. or less below the standard figures are examined with the Hortvet cryoscope, and are frequently found to be substantially adulterated.

STEROL ACETATE TEST FOR GHEE.—Different Provinces in India have prescribed standard Reichert values for ghee, ranging from 22 to 30, with which all samples must comply. Actually, genuine ghee commonly gives figures ranging from 20 to 40, though most samples show a more restricted range. In Bombay a minimum Reichert value of 24 is prescribed; all samples giving figures below this are condemned automatically, and the analyst is entitled to pass samples giving a higher figure. In the Madras Laboratory the sterol acetate test, carried out as described in THE ANALYST (1933, 58, 529), is applied to all doubtful samples. Of 376 samples giving Reichert figures between 20 and 24, the test enabled 242 to be classified as genuine and 134 as adulterated, while 70 samples showing figures above 24 were classed as adulterated.

DETENTION OF FOOD HAWKERS.—In 82 cases proceedings against food hawkers had to be abandoned, as the vendors could not be traced. To overcome this difficulty, a provision was inserted in the Public Health Act (Sec. 140) giving an inspector power to detain anyone committing an offence until his identity was satisfactorily established. In practice this provision has been found of little value, because an inspector is unable to tell whether a hawker is selling genuine food or not until he receives the certificate of analysis. This difficulty might be met in

another way. Section 258 of the District Municipalities Act requires that vendors of dairy produce, including hawkers, should be licensed. In most municipalities this section, so far as it applies to hawkers, is a dead letter. If it were operative and hawkers were required to carry a licence, then section 140 of the Public Health Act could be used, as an unlicensed hawker would *ipso facto* be committing an offence and could be held in custody while his identity was being established.

LEAD IN CURRY POWDER.—As the result of English importers insisting on a certificate that curry powder imported into England does not infringe the limit fixed for lead in foods, a number of these powders have been examined. Of 13 samples received from private firms in Madras, 4 contained more than 10 p.p.m., 5 between 5 and 10 p.p.m., and 4 less than 5 p.p.m. A certificate was given when the proportion of lead was less than 5 p.p.m.

DIFFERENTIATION OF HAND-POUNDED FROM MILLED RICE.—It has been prescribed by the Government that hand-pounded rice should be used in hospitals. Of 66 samples received, 35 proved to be milled. When the Order first came into force, the samples examined were almost invariably prepared by milling, whether sold as hand-pounded or not, but owing to adverse reports most samples are now satisfactory.

The following simple method of distinguishing between hand-pounded and milled rice has been worked out by K. V. Sundaram Ayyar, M.Sc., A.I.C. (Senior Assistant to the Government Analyst):—As much rice as will lie on the bottom in one layer, but without completely covering the surface, is put into a 50-ml. beaker. Fifteen ml. of a 5 per cent. aqueous solution of sodium hydroxide are added, and the mixture is stirred by rotating the beaker and then left for about 30 seconds. When the beaker is again shaken with a rotatory motion the particles of rice move about freely if they are hand-pounded, but stick together, or to the bottom of the beaker, if milled.

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1939

THE Chemical Examiner's Department, which is a branch of the Education and Public Health Department, is under the direction of Dr. S. Rajagopal Naidu, M.B.E., M.B., B.S., F.I.C. The work comprises toxicological investigations, stain cases and miscellaneous medico-legal work, including the examination of firearms, bones and tissues, counterfeit coins, stamps, documents, etc. The total number of articles examined was 9392, as compared with 8913 in 1938.

HUMAN POISONING CASES.—Of the 458 cases investigated, poison was detected in 250, comprising 91 inorganic and 159 organic poisons. Oleander headed the list with 30 cases and datura and opium came next, with 29 and 25 cases respectively. Alcohol was found in 16 exhibits, aconitine in 18, madar juice in 13, nux vomica in 5, and oduvan in 6. Among the inorganic poisons, copper sulphate was identified in 27 cases, potassium or sodium nitrite in 13, mercury in 17, arsenic in 14, sulphuric acid in 9, and cyanide in 5.

Holarrhena antidysenterica, Wall.—This plant, commonly known as "kurchi" or "conessi," is a small deciduous tree with white flowers growing throughout the forests of India. Recent clinical experience has shown that it is a valuable antidysenteric drug. It contains alkaloids which are known to be poisonous. Two children were given the bark of this plant as a purgative, and both died. The post-mortem examination revealed cardiac failure, the heart being distended with dark fluid blood. The specimen of the plant submitted yielded an alkaloidal extract, which killed frogs with paralysis and gave the following chemical reactions: (1) with sulphomolybdic acid a dark green colour; (2) with sulphovanadic acid a greenish-brown colour changing to purple at the edges; (3) with formaldehyde and sulphuric acid (Marquis' reagent) a reddish-brown colour turning blue at the edges. An alkaloidal extract giving these reactions was also obtained from the viscera of each of the children.

Nitrites.—Both potassium and sodium nitrite are extensively used by weavers in the dyeing of cloths in villages and can be bought without restriction. Cases of nitrite poisoning have therefore become increasingly frequent in recent years. The fatal dose for frogs is about 1 mg. of nitrite ion per 10 g. of body weight, and the fatal dose for dogs is similar, whether injected or administered by the mouth. The fatal dose for an average adult man, calculated by Meeh's formula (*cf. Extra Pharmacopoeia, Martindale*, 21st Ed., Vol. I, p. xxxii), would probably be 30 grains of sodium nitrite or 40 grains of potassium nitrite. A regular feature in animals killed by nitrite poisoning is the presence of methaemoglobin in the blood taken from the heart after death. When the poison is administered by the mouth most of it is rapidly absorbed and otherwise destroyed, and very little is left in the viscera. Hence in cases of human poisoning only small quantities of nitrite can be detected in the viscera unless very large doses have been swallowed.

ANIMAL POISONING CASES.—Of the 23 cases investigated, poison was detected in 13. Arsenic was found in 5 cases, oleander in 6, madar juice in 1, and a mixture of arsenic, mercury, copper, nux vomica seeds, aconitine, datura seeds and castor seeds in 1.

TATTOO MARKS.—Among the miscellaneous cases was one in which a man, accused of murder, was alleged to have cut the body of the victim into several pieces and to have buried them in a river bed. Some of these portions were recovered by the police, and on one of these pieces there were letters which appeared like tattoo marks corresponding to the name of the deceased. The problem submitted was to decide whether these letters were tattoo marks or merely writing in ink.

The characters were not affected by water, acetic acid, oxalic acid, ammonia, bleaching powder or potassium cyanide. A cross section of the skin showed dense fibrous tissue with superficial intracellular dark brown amorphous pigment. It was therefore concluded that the letters on the skin were tattoo marks and not surface writing.

ALTERATIONS ON A DOCUMENT.—A village officer was ordered to hold the elections for a panchayat board. It was suspected that he had not held these elections, but had reported falsely that he had done so on September 28th, 1938, and had subsequently tampered with the notice by altering the date and day of the week. Examination of the document by ordinary and ultra-violet light showed two places in ink of a deeper shade than on the remainder of the paper. It was also revealed that the figures and word of the date overlapped those of a date which had originally been November 5th, 1938.

RE-USED POSTAGE STAMPS.—Partly erased and re-used postage stamps are frequently submitted for identification of the erased postal impression. For this purpose Cellophane paper is very useful. The postal impression is printed on the transparent paper and can be superimposed on the suspected stamp. A complete coincidence of the circles and other marks that have not been erased enables a conclusion to be drawn.

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(Supplementing the series published in the ANALYST up to 1933, **58**, 340, and bringing the Bibliography up to date.)

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E. B. D.

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Food and Drugs

Hydrogen Sulphide in Corned Beef. A. Elias. (*Indust. y. Quim.*, 1940, **3**, 31–32.)—The presence of small amounts of hydrogen sulphide in Argentine corned beef has been reported. To discover its origin, 20 g. of the samples were treated with 50 ml. of 10 per cent. sulphuric acid, and the hydrogen sulphide evolved was estimated colorimetrically by comparing the stains produced on lead acetate paper in the course of 24 hours with standards prepared from sodium sulphide of known purity. It was found that a faint reaction was obtained with 0·00187 mg. of hydrogen sulphide, and this was taken as the lowest limit. The most constant results were obtained by using only 1 g. of the sample of beef. Freshly killed meat yielded traces of hydrogen sulphide (about 0·05 mg. per 100 g.), but this disappeared after the sample had been kept in a refrigerator for 48 hours. On the other hand, a sample of corned beef which had been sterilised for 2½ hours at 113° C. yielded 3·74 mg. per 100 g. It is recommended that an effort should be made to reduce the decomposition of the proteins to a minimum, so that the amount of hydrogen sulphide should not exceed the 0·05 mg. per 100 mg. present in the fresh meat.

Detection of the Bleaching of Flour with Chlorine. D. B. Scott. (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 675–678.)—The following method for the determination of chlorine in the fat of flour has been proposed (Scott, *J. Assoc. Off. Agr. Chem.*, 1940, **23**, 497). The flour (500 g.) is shaken at five-minute intervals for 30 minutes with 700 ml. of petroleum spirit, the mixture is filtered by means of a Buchner funnel, and the filtrate is passed through the flour a second time to ensure freedom from suspended flour, and is then concentrated to 10 ml. and treated by one of the following methods. By the "quick ash method" the extract (10 ml.) is added to 15 g. of fusion mixture (138 g. of anhydrous potassium carbonate, 106 g. of anhydrous sodium carbonate and 75 g. of potassium nitrate) which is then dried and weighed to determine the amount of fat added. A further 5 g. of fusion mixture is spread over the surface, and the mixture is ignited to a white ash at 525° to 600° C. The residue is treated with 25 ml. of hot water and rinsed into a 200-ml. beaker with hot water, acidified to litmus paper with nitric acid, treated with a further 25 ml. of nitric acid and 5 ml. of 0·3 *N* silver nitrate solution and boiled for 5 minutes. The solution is filtered through a chlorine-free paper, which is washed with 1 per cent. nitric acid, and the A.O.A.C. method is then followed, beginning at the words "place the paper in a Kjeldahl flask. . . ." By the "acid digestion method" the extract is evaporated to dryness, the fat is weighed and treated with 5 ml. of 0·3 *N* silver nitrate solution and 25 ml. of nitric acid, and the volume of liquid is reduced to about 10 ml. While the liquid is briskly boiling, nitric acid is added, a few ml. at a time, until the fat is completely destroyed, after which an equal volume of water is added and the liquid is boiled for 5 minutes and filtered. The A.O.A.C. method is then followed from the point previously indicated. The fat of the flour should be subjected to a preliminary Beilstein test for chlorine, and if this indicates a high content the amount of sample should be reduced to 200 g., and 300 ml. of petroleum spirit should be used for extraction. The application of the method to the determination of known amounts of sodium chloride added to 4 g. of olive oil showed that no chlorine is lost in the process. The chlorine found in the fat of unbleached flour ranged from 0·03 mg. to 0·19 mg. per g. of fat. Flours bleached with chlorine and nitrosyl chloride gave 10·3 to 18·9 mg. per g. From the results it may be concluded that chlorine in excess of 0·25 mg. per g. of fat indicates that the flour has been treated with bleaching preparations. The average chlorine-content of 28 authenticated samples of unbleached flour was 0·11 mg. per g. of fat. A. O. J.

Copper in Tomatoes. W. J. Shannon and D. T. Englis. (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 678–680.)—Samples of several varieties of tomatoes, obtained from different growers in central and northern Illinois and subject to the effect of different types of soil and other factors, were examined for their copper-content. The tomatoes were washed twice with distilled water, rinsed once with copper-free water, and then pulped in a food chopper, only the stems being excluded. The material was prepared for analysis by oxidation with nitric and perchloric acids (Gieseking, Snider and Getz, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 185). The copper was estimated with the sodium diethyldithiocarbamate reagent, a single cell photoelectric colorimeter and a blue filter being used, as recommended by Drabkin (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 320). The calibration curve in the range of concentration studied was constructed by means of solutions of pure copper sulphate. The results showed that the average copper-content of tomatoes from these regions ranged from 15 to 25 parts per million. A. O. J.

Macaúba Oil (Mocaya). M. Silva. (*Indust. y Quim.*, 1940, **3**, 39–41.)—According to some authors, macaúba oil is derived from the palm *Acrocomia sclerocarpa*, but Bolton states ("*Oils and Fatty Foods*," p. 176) that it is obtained from *Acrocomia totai*. A sample extracted

from nuts from Minas-Geraes gave the following values: sp.gr. at 15° C., 0·9212; n_D^{15}, 1·4631; m.p., 23·6° C.; solid. p., 18·3° C.; acid value, 3·40; saponification value, 239·70; iodine value (Hanus), 22·6; glycerol (calc.), 12·76.

Component Glycerides of a Typical Cow Milk Fat. T. P. Hilditch and S. Paul. (*J. Soc. Chem. Ind.*, 1940, **59**, 138–144.)—The method of separation of fats by preliminary crystallisation from acetone into one or more fractions, the component glycerides of which can be determined within fairly near limits, has now been extended to a typical butter-fat produced by cows at summer pasture. At least 4 main groups of acyl compounds have to be considered: palmitic, stearic, oleic with octadecadienoic and traces of unsaturated C_{20} and C_{22} acids, and the separate group of characteristic milk-fat lower saturated acids from butyric to myristic, with traces of decenoic, do- and tetra- decenoic acids, so that final deductions are less certain than with simpler fats and necessitate the grouping together of all the lower acids below C_{16}. The original butter-fat was separated into three fractions, and their component acids were determined by ester fractionation; the fully saturated glycerides were determined and isolated, and, when possible, fractionated by crystallisation and the component acids determined; the completely hydrogenated fraction was separated by crystallisation from acetone or ether followed by component acid analysis of each hydrogenated fraction obtained. The mixed glycerides (per cent. mol.) were probably in the neighbourhood of "oleo"-mono-C_{4-14} palmitins 31–22, "oleo"-palmitostearins 8–17, palmitodi"oleins" 17–4, "oleo"-mono C_{4-14} stearins 12–6, smaller proportions of "oleo"-di C_{4-14}, 4–9, mono C_{4-14} di"oleins" nil-10, stearodi"oleins" 8–1, and "oleo"-dipalmitins, 1–5; tri-"oleins," nil–7 (very probably mainly octadecadienodiolein), and fully saturated glycerides (mono-C_{4-14}-palmitostearins 9, di-C_{4-14} palmitins 6–7, and small amounts of di-C_{4-14}-stearins, mono-C_{4-14}-palmitins, dipalmito stearins and palmitodistearins) amounting in all to 19 per cent. mol. Glycerides containing one radical each of oleic, palmitic, and one of the lower acids are most abundant (22–30 per cent. of the whole fat), whilst nearly 40 per cent. of the fat is made up of the four groups "oleo"-mono-C_{4-14}-palmitins, "oleo"-palmitostearins, palmitodi"oleins" and "oleo"-mono-C_{4-14} stearins, and 19 per cent. of fully saturated glycerides are present. Palmitic acid is combined with other acids in about 70 per cent. of the butter glyceride molecules, and there is a similar distribution in the depôt fat of the cow. It is suggested that butter-fat may be the result of transformation of preformed oleoglycerides in the mammary gland, and the relative distribution of the lower fatty acids and of stearic acid are discussed in this relation. D. G. H.

Detection of Adulteration in Ghee by a Study of its Fluorescence. G. Narasimhamurty and V. V. Suryanarayanamurty. (*Current Science*, 1940, **9**, 334–336.)—Jha (*J. Ind. Chem. Soc., Ind. & News Ed.*, 1939, **1**, 159) has described a qualitative test for the adulteration of ghee, which depends on its fluorescence in ultra-violet light, and Muthanna and Mukerji (*Current Science*, 1940, **9**, 120) have evolved a similar quantitative method, in which a Pulfrich photometer is used to measure the intensity of the fluorescence and to obtain standard curves for the common adulterants of ghee. Earlier work has suggested that such methods might be influenced by the age of the sample and the presence of artificial colours. Tests were therefore made in which the intensity of the fluorescence produced by the ultra-violet light transmitted by filters that allow the passage of radiations of wave-lengths 520 to 540 and 450 to 490$m\mu$ (which are regarded as characteristic of ghee and its adulterants) was measured in a Pulfrich photometer. A solution containing 880γ of quinine per litre was used in a similar way as standard, and the solution tested contained 1 vol. of the melted fat and 3 vol. of chloroform. The results show that a combination of the blue fluorescence of crude groundnut oil and the yellow fluorescence of a colouring matter which is commonly used in the dairy industry for adding to butter, can simulate the greenish fluorescence associated with genuine ghee. The ratio of the intensities of the blue and green components of the fluorescence indicated no relationship with factors such as the age and purity of the sample. J. G.

Neutralisation Value of Ghee (Butter-fat). H. Hawley. (*Current Science*, 1940, **9**, 337–339.)—The Reichert value is unsatisfactory as an indication of adulteration of ghee, because the herds of animals (usually buffaloes) from which it is obtained are subjected to very variable climatic and feeding conditions, and the composition of the butter-fat varies accordingly, resulting in Reichert values ranging from less than 20 to over 40. Tests which depend on the butyric acid content are also unreliable, because they do not make it possible to decide whether a low Reichert value is due to abnormality or to adulteration with a fat which contains no butyric acid. Other tests (*e.g.* the saponification value, the n_D or the sterol acetate test) also have their limitations. The neutralisation value (*N.V.*) of the fatty acids is of greater use if determined by the author's method, which minimises losses of volatile acids (*e.g.* caproic and caprylic acids); it does not include the butyric acid, which is soluble in water. About 10 g. of the clear fat are saponified with 150 ml. of water and 30 ml. of a solution of 84 g. of sodium hydroxide in 210 ml. of water, to which is added sufficient glycerol to make 1 litre. This mixture is heated on a water-bath in a 500-ml. flask fitted with an 8-inch air-condenser, the top of which is covered with an inverted test-tube. When hot, the contents of the flask are acidified with

10 ml. of approximately 17 per cent. (by vol.) sulphuric acid, the strength of which has previously been adjusted (as the result of a blank titration with methyl red as indicator), so that 9·0 to 9·5 ml. serve to neutralise the alkali present. After 3 hours (not more) on the water-bath, with frequent shaking, the fatty acids are clarified, and 50 ml. (which includes all or most of the fatty acids) are poured off and washed with three 25-ml. portions of hot water in a separating funnel. The acids are filtered (in a steam oven), and about 5 g. of the filtrate are pipetted into a tared flask and weighed (to within 2 mg.). They are then dissolved in 50 ml. of 90 per cent. alcohol (which has previously been neutralised to thymol blue), and the solution is titrated with a freshly made 0·5 *N* solution of sodium hydroxide, with 1 ml. of 0·04 per cent. thymol blue solution as indicator, until the yellow colour has changed to a slate-green shade. The *N.V.* is then the number of mg. of potassium hydroxide required to neutralise 1 g. of fatty acid; duplicates should agree to within 0·2. Results tabulated for 78 samples showed that, although there is some tendency for high Reichert values to be associated with high neutralisation values, they do not run parallel with one another in the way that the former does with the saponification value. It is suggested that a sample of bulked ghee which has a *N.V.* of less than 209 is almost certainly adulterated, and that if the *N.V.* is less than 210 the sample must be regarded with suspicion. Of 7 samples which gave a positive sterol acetate test, 5 could have been condemned on the *N.V.* alone, whilst one had a *N.V.* of 209 to 210, and there was reason to believe that adulteration of the other was only slight. Of 10 remaining samples, none of which contained vegetable fat, 2 were classed as adulterated, 1 as doubtful, and the others as genuine. Incidentally, a substitute for the sterol acetate test is an advantage in view of the present difficulty of obtaining digitonin. J. G.

Lower Saturated Fatty Acids in Herring Oil. H. Nobori. (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 110B.)—About a ton of the mixed fatty acids of herring oil (neutralisation value 197·3, saponification value 199·0, iodine value 128·9) was distilled in a commercial plant, and 28·5 per cent. of the lower-boiling fraction (205–217° C. at 12–10 mm.), with neutralisation value 221·1, saponification value 220·9 and iodine value 76·9, were obtained. This fraction contained lauric acid (2·2 per cent.) and capric and caprylic acids (0·9 per cent. of the original mixed fatty acids). Physeteric acid ($C_{14}H_{26}O_2$) is regarded as a constituent of the unsaturated acids, and a hydrocarbon, pristane, as a main constituent of the unsaponifiable matter of the fraction of lower b.p. D. G. H.

Selective Action of Fatty Acid on the Ethanolysis of Sardine Oil. M. Takano, M. Takao and M. Danjo. (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 132–133B.)—The refined oil was mixed with an equal volume of 0·5 *N* sodium hydroxide solution in 95 per cent. alcohol, the mixture was shaken vigorously at 20° C., and the resulting products were taken from the reaction mixture during the course of ethanolysis. The reaction ceased on addition of dilute hydrochloric acid, and some free fatty acids were liberated from the soap produced. Samples were washed with hot water and each was assumed to consist of tri-, di- and mono- glyceride, free fatty acids and ethyl ester. The products were then distilled under 2–3 mm. pressure to separate ethyl esters, and the samples showed increasing free fatty acidity; hence the alkali for saponification can be only a small portion of that used, and most of it probably acts as catalyst for the ethanolysis. The distillate and residue were also analysed. The high acetyl values of the residues show that di- or mono- glyceride may be produced in ethanolysis. The saponification value of the distillate is generally higher than that of the residue and the iodine value lower, so that the fatty acids of lower molecular weight and those of less saturation may react more rapidly. The distillate and residue were treated by the lithium salt and acetone method to separate unsaturated fatty acids, and the residue was further separated into solid and liquid fatty acids by the lead salt procedure. Results of analysis are given. Solid fatty acids react to the greatest extent, liquid (less unsaturated) acids come next, and highly unsaturated react least. Further, the saturated acids of lower molecular weight tend to react more rapidly than the other solid acids; of the highly unsaturated acids, and even of the liquid acids, those with high neutralisation values react more rapidly than the others. D. G. H.

Determination of Mercury in Mercurochrome. G. J. W. Ferrey. (*Pharm. J.*, 1940, **144**, 366.)—In the B.P. method the mercury in mercurochrome is determined in acid solution, and a large proportion of alcohol is required to keep dissolved the dibromohydroxymercurifluorescein that is formed; the results may be low and erratic. The following method, which can be carried out in 30 minutes, gives consistent and accurate results:—A weighed quantity (0·5 to 1 g.) of the sample is dissolved in 20 ml. of water, and the solution is treated with 5 g. of potassium hydroxide pellets and 2 g. of zinc filings and boiled under reflux for at least 15 minutes. The condenser is then washed down with 50 ml. of water, and the amalgam is separated by decantation, washed well with water, and dissolved in a mixture of 20 ml. of nitric acid and 20 ml. of water. The solution is gently boiled until nitrous fumes cease to be evolved, treated with a slight excess of permanganate, decolorised with a drop of hydrogen peroxide solution, and titrated with *N*/10 ammonium thiocyanate solution.

The Bambarra Groundnut or Njugo Bean. J. M. Holm and B. W. Marloth. (*Dept. of Agric. and Forestry, South Africa, Pamphlet No.* 215, 1940, 1–10.)—The Njugo bean (*Voandzeia subterranea*) is widely cultivated throughout tropical Africa, and Bambarra (a district near Timbuctoo) has no pre-eminent claim to the plant. It is also extensively grown in the Transvaal, Natal and Zululand. It resembles the ground-nut (*Arachis hypogaea* L.) only in so far as it matures its seed in a pod underground. Several varieties, distinguished mainly by the colour of the shelled seed, are recognised by the natives. An analysis of the dehusked beans by D. C. Crawford gave the following results: moisture, 10·3; protein (N × 6·25), 15·0; fat, 7·4; fibre, 5·1; carbohydrates, 59·1; ash, 3·1; phosphoric oxide, 0·6; potash, 1·1. The following table gives the percentage composition of green and ripe nuts, as determined at the Station Agronomique, Mauritius.

	Water	Protein (N × 6·25)	Fat	Fibre	Carbohydrate	Ash
Nuts (green)	58·5	7·3	3·2	3·0	26·4	1·16
Shells (green)	80·3	1·6	0·1	5·5	11·7	0·8
Entire fruits (green) ..	63·6	6·02	2·43	3·58	23·13	1·46
Nuts (ripe)	12·5	14·7	6·1	5·7	57·1	3·9
Shells (ripe)	11·1	7·3	0·8	29·1	47·8	3·9
Entire fruits (ripe) ..	12·27	13·36	5·17	9·86	55·4	3·94

Composition of Certain Nutshells. M. Phillips and M. J. Goss. (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 662–665.)—The percentage compositions of the following nutshells were determined:—Almond (*Amygdalus communis*), Brazil nut (*Bertholletia excelsa*), candle nut (*Aleurites moluccana*), coconut (*Cocos nucifera*), English walnut (*Juglans regia*), filbert (*Corylus avellana*), and pecan (*Hicoria pecan*). The shells were ground to pass through a 60-mesh sieve and dried at 105° C. Ash was determined by ignition at 600° C., nitrogen by the Kjeldahl-Gunning method, methoxyl by the method previously described (Phillips, *J. Assoc. Off. Agr. Chem.*, 1932, **15**, 123; Abst., ANALYST, 1932, **57**, 402), and extractives by the method of Phillips *et al.* (*J. Agr. Res.*, 1939, **59**, 319). Uronic acid anhydrides were determined in the unextracted material by the method of Dickson, Ollerson and Link (*J. Amer. Chem. Soc.*, 1930, **52**, 775) as modified by Phillips, Goss and Browne (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 289; Abst., ANALYST, 1933, **58**, 495), furfuraldehyde by the method of the A.O.A.C. and crude cellulose by the method of Kürschner and Hanak (*Z. Unters. Lebensm.*, 1930, **59**, 484). Pentosans and lignin were determined by methods previously described (*cf.* refs. pp. 324, 326, *J. Assoc. Off. Agr. Chem.*, 1940, **23**). The figures found for ash and nitrogen were low except for candle nut (ash, 3·64 per cent.). The percentages of methoxyl were somewhat higher than those found in lignified plant materials, and ranged from 5·29 (almond) to 7·14 (walnut). The percentages of alcohol-benzene extractives were rather low, but those of other extractives as well as of the uronic acids were of the order usually found for lignified substances. The percentages of pentosans were generally higher in materials of low lignin-content and *vice versa*, although this relation was neither regular nor proportional. The percentages of lignin in candle nut (37·29) and pecan (35·51) were unusually high, higher even than those for such highly lignified material as woods (*cf.* Fleck, Van Beckum and Ritter, *J. Amer. Chem. Soc.*, 1937, **59**, 2279; Abst., ANALYST, 1938, **63**, 66). Where the percentage of lignin was high the percentage of methoxyl in lignin was somewhat low (*e.g.* candle nut 12·03; pecan, 11·03). Almond shells with a low percentage of lignin (17·13) gave 17·54 per cent. of methoxyl in "pure" lignin. The figures for cellulose and crude cellulose showed little variation in the kinds of shells examined.

A. O. J.

Phenol and Eucalyptus Ointments. H. Brindle. (*Pharm. J.*, 1940, **145**, 20.)—Experiments on the preparation and storage of these ointments show that the loss of phenol in preparing about 250 g. of phenol ointment by ordinary methods is approximately 5 per cent. If the ointment is stored in collapsible tubes the loss is negligible, even after a year or more; in well-closed containers the loss in 9 months may reach about 8 per cent., but it can be kept down to much less. The loss in preparation is about 1 to 2 per cent. at 60° C. and 5 per cent. at 80° C. In full, well-closed containers the loss of oil on storage for 18 months and for 3 years was only about 2 to 3 per cent. It is concluded that the most satisfactory way of dealing with ointments containing volatile ingredients is to purchase them in collapsible tubes. Such ointments should not be stored in the usual shop jar with a loosely fitting cover. If kept in airtight containers, particularly if well filled, there should be no danger of trouble with the authorities if the samples are not stored for more than 1 or 2 years. The ointments may be prepared freshly as required. It is possible that the efficiency of collapsible tubes is not altogether due to their being airtight, as stoppered bottles show a loss, but largely due to complete filling preventing condensation on the sides of the container. E. M. P.

Biochemical

Determination of Carotene in Presence of Lycopene. G. S. Fraps, A. R. Kemmerer and S. M. Greenberg. (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 422–425.)—Impurities occurring in crude carotene solutions can be removed to some extent by means of magnesium carbonate specially prepared so as to adsorb

crude xanthophyll but not carotene, and called the xanthophyll reagent (*cf.* Fraps and Kemmerer, *J. Assoc. Off. Agr. Chem.*, 1939, **22**, 190; Abst., ANALYST, 1939, **64**, 369). Some foods (*e.g.* tomato, water melon, red pepper) contain lycopene or other red pigments which are not completely adsorbed by the xanthophyll reagent. Experiments were made to devise a method of preparation of a reagent that would adsorb lycopene but not carotene. A test solution of crude lycopene was prepared by refluxing 100 g. of canned tomato pulp for 30 minutes with 250 ml. of saturated alcoholic potassium hydroxide solution. The carotene fraction, containing lycopene, was extracted by means of petroleum spirit as in the Hughes Peterson modification of the Guilbert method (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 79), and the extract was washed with 90 per cent. methanol to remove xanthophyll, then with water to remove residual methanol, and finally dried over sodium sulphate. The solution was diluted to 200 to 400 ml. with petroleum spirit and shaken with 50 g. of the xanthophyll reagent. The filtrate was treated gradually with a preliminary preparation of magnesium carbonate that would adsorb lycopene without adsorbing carotene. The adsorbent was filtered off and washed with petroleum spirit, and the purified lycopene was eluted from the magnesium carbonate with petroleum spirit containing 2 per cent. of ethanol. The eluate was washed free from alcohol, dried over sodium sulphate, and made up to a colour strength equivalent to 0·5 to 0·8 p.p.m. of carotene. Lycopene solutions thus prepared are unstable, even when kept in the dark in cold storage, and should be freshly prepared every week. To test the reagent, the colours of test solutions of lycopene and carotene were read in a KWSZ photometer before and after treatment of 50 ml. of each with 3 to 5 g. of the reagent. To be satisfactory the reagent must adsorb all the lycopene from a solution containing 0·5 to 0·8 p.p.m. of lycopene, and no carotene from a solution containing the same amount of carotene. Xanthophyll will also be adsorbed by the lycopene reagent. After a number of trials a lycopene reagent was prepared as follows:—Magnesium carbonate (100 g.) was heated in an electric furnace at 200° C. for 1 hour and then tested for adsorption of carotene. If the reagent did not adsorb carotene it was tested with the lycopene solution, and, if 3 to 5 g. of the reagent extracted all the red pigment from 50 ml., it was ready for use. If the reagent adsorbed carotene, water was added in 3-ml. portions until there was no further adsorption. It was then tested with the lycopene solution. Some modification of the procedure (*e.g.* longer heating) may be necessary with different specimens of magnesium carbonate. The lycopene reagent removed 76·7 per cent. of impurity from crude carotene in solutions derived from water melons, compared with 8·3 per cent. by the xanthophyll reagent. From carotene derived from dried apricots the lycopene reagent removed 31 per cent. of impurity and the xanthophyll reagent 8·6 per cent. The crude carotene from tomato, red pepper and alfalfa also yielded more impurity to the lycopene reagent than to the xanthophyll reagent.

A. O. J.

Adsorption Method for the Determination of Pure Carotene. G. S. Fraps, A. R. Kemmerer and S. M. Greenberg. (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 659–662.)—In the tentative method of the A.O.A.C. for the determination of carotene (*J. Assoc. Off. Agr. Chem.*, 1939, **22**, 79) the material is boiled with alcoholic potassium hydroxide solution, petroleum spirit is added, the resulting mixture is diluted with water and the petroleum spirit layer is removed and washed with water and then with dilute methyl alcohol. The method might be shortened by treating the petroleum spirit extract with xanthophyll adsorbent (*cf.* preceding abstract) immediately after it has been washed with water, the washing with methyl alcohol being omitted. An investigation of this procedure showed that more washings with water were required to remove the alkali than were necessary when methyl alcohol was used, but that the alkali could be effectively removed by a final washing with dilute hydrochloric acid. The method finally used was as follows:—The sample (1 to 6 g.) was extracted with 20 to 120 ml. of saturated alcoholic potassium hydroxide solution as in the A.O.A.C. method (*loc. cit.*). The extract was diluted, and the carotinoid pigments were extracted with petroleum spirit, which was washed three times with water and once with a 0·5 per cent. solution of hydrochloric acid. The solution was dried over anhydrous sodium sulphate and diluted to 200 ml., and about 100 ml. were shaken for one minute with 8 g. of the xanthophyll adsorbent. The clear solution was examined in a photoelectric colorimeter, and the solution was again treated with 4 g. of the adsorbent, the treatment being repeated until no more colour was removed. If the material contained lycopene, the lycopene adsorbent was used (*cf.* the preceding abstract). The method was applied to 19 samples, and the shorter method gave the same results as the longer modified A.O.A.C. method. A. O. J.

Colorimetric Assay of Weakly Phenolic Ketones, "Oestrone," in Extracts of Human Urine. N. B. Talbot, J. K. Wolfe, E. A. MacLachlan, F. Karush and A. M. Butler. (*J. Biol. Chem.*, 1940, **134**, 319–330.)—A 24-hour sample of urine, containing 7 ml. of hydrochloric acid as preservative, is hydrolysed, within 12 hours of collection, by boiling under reflux for exactly 10 minutes with 15 per cent. of hydrochloric acid by vol. The liquid is then cooled and extracted 4 times with one-fifth of its volume of ether. The combined ethereal extracts are washed with 20 ml. of 20 per cent. sodium carbonate solution, evaporated to 100 ml., and transferred quantitatively to a separating funnel; the volume is adjusted to about 190 ml. The ethereal solution is washed alternately with

three 25-ml. portions of 0·1 *N* sodium hydroxide solution and two 25-ml. portions of 0·1 *N* sodium hydroxide—sodium hydrosulphite reagent (prepared immediately before use by adding 50 ml. of 0·1 *N* sodium hydroxide solution to 5 g. of sodium hydrosulphite) to remove strongly acidic and phenolic substances. In extracting with the hydrosulphite solution the funnel should be shaken thoroughly for at least 3 minutes. The ether is next washed twice with 25-ml. portions of 0·5 *N* hydrochloric acid and three times with 25-ml. portions of water; all the washings are discarded. The ethereal solution is then evaporated almost to dryness, and the residue is transferred to a 250-ml. separating funnel by means of four 25-ml. portions of toluene. The weakly phenolic substances are extracted from this solution with four 25-ml. portions of *N* sodium hydroxide solution, and the combined extracts are made acid to Congo red with hydrochloric acid and then adjusted to a *p*H that is acid to litmus and alkaline to Congo red by adding 20 per cent. sodium carbonate solution. The solution is extracted with five 40-ml. portions of ether, and the combined ethereal extracts are washed successively with 25 ml. of 0·1 *N* sodium hydroxide solution, 2·5 ml. of 0·1 *N* sodium hydroxide—sodium hydrosulphite reagent (shaking for at least 3 minutes), 25 ml. of 0·1 *N* sodium hydroxide solution, two 25-ml. portions of 0·5 *N* hydrochloric acid and three 25-ml. portions of water. The ethereal solution is evaporated to dryness, and the residue is transferred with four 1-ml. portions of absolute alcohol to a small Pyrex vessel graduated at 4 ml. and fitted with an all-glass reflux condenser. After addition of 0·5 ml. of glacial acetic acid and 0·5 g. of Girard's reagent T (betaine hydrazide hydrochloride, stored in a vacuum desiccator over conc. sulphuric acid) to the alcoholic solution, it is heated under reflux for half-an-hour and, after cooling, transferred with the aid of 40 ml. of ice-cold water to a separating funnel. Three ml. of 10 per cent. sodium hydroxide solution are added, and the solution is extracted with four 40-ml. portions of ether; the ethereal extracts are discarded. The aqueous solution is run into a flask containing 1 ml. of conc. sulphuric acid diluted with 60 ml. of water, and the liquid is transferred to a separating funnel. Forty ml. of ether are added, and the mixture is allowed to stand at room temperature for 75 minutes and then shaken. The ethereal extract is removed, and the aqueous solution is re-extracted with four further 40-ml. portions of ether. The combined ethereal extracts are washed with 25 ml. of 0·1 *N* sodium hydroxide solution, followed by three 25-ml. portions of water, and evaporated to dryness, and the residue, containing the weakly phenolic ketones, is dissolved in 1 to 4 ml. of absolute alcohol. An aliquot portion (0·3 ml.) of the solution is transferred to a small dry test-tube and mixed with 0·75 ml. of 2 per cent. sodium carbonate solution. Wetting of the upper walls of the test-tube must be avoided during this operation. A solution (0·1 ml.) of diazotised dianisidine* is added as rapidly as possible, with stirring, followed one minute later by 0·8 ml. of toluene. The tube is shaken vigorously and then centrifuged together with a blank prepared in the same way, but containing no hormone. Aliquot portions (0·6 ml.) of the clear coloured toluene solutions are transferred from the tubes to the 1-ml. cells of a photoelectric colorimeter, and the galvanometer readings are taken with filter 420. The results (in γ of weakly phenolic ketones, "oestrone") are calculated either from a standard curve prepared with solutions of crystalline oestrone of known dilution, or from the expression (2 — log G)/K, where K is the "proportionality constant" determined from solutions containing known amounts of crystalline oestrone and G is the galvanometer reading of the unknown. Crystalline oestrone can be estimated with an error of approximately 10 per cent. An average recovery of 72 per cent. of crystalline oestrone in pure solutions was obtained in the purification of extracts up to treatment with Girard's reagent T, and an average recovery of 95 per cent. of crystalline oestrone in the ketonic fraction after treatment with that reagent. When crystalline oestrone was added to the crude ethereal extracts of hydrolysed urine, recoveries averaging 65 per cent. were obtained, comparable with an average recovery of 67 per cent. with pure solutions for the complete purification procedure. F. A. R.

Thiochrome Method for the Estimation of Aneurin, with Survey of the Aneurin Content of Wheats. R. G. Booth. (*J. Soc. Chem. Ind.*, 1940, **59**, 181–184T.)—Pyke's method (this vol., 180) is considered to be the most suitable modification of Jansen's reaction (ANALYST, 1937, **62**, 60) for the estimation of aneurin in wheat, but it is open to

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*To 10 g. of crude dianisidine (m.p. 134·5 to 136·5° C.) are added 140 ml. of water and 6 ml. of conc. hydrochloric acid, and the mixture is boiled until the solid dissolves completely. The boiling is continued for a further 5 minutes after addition of 0·5 g. of stannous chloride, and the solution is finally decolorised by adding 1 g. of Norit A. The filtrate is treated with 50 ml. of conc. hydrochloric acid and cooled, and the purified dianisidine dihydrochloride, m.p. 283° C. (decomposition), is filtered off, washed with ethyl alcohol, and dried in a vacuum desiccator over sodium hydroxide until free from hydrochloric acid. Three ml. of water, followed by 0·3 ml. of conc. hydrochloric acid, are added to 25 mg. of dianisidine dihydrochloride, and the solution is treated with 0·6 ml. of freshly prepared 5 per cent. sodium nitrite solution. After 5 minutes 0·6 ml. of 5 per cent. urea solution is added, and the solution is allowed to stand for another 5 minutes until all the bubbles of gas have escaped. The reagent is stable for 6 days if stored in the dark.

criticism in that it is assumed that the predigestion process proceeds to completion, although this never occurs in practice and, indeed, is theoretically impossible. This difficulty, however, may be overcome by adding a known amount of aneurin to a separate portion of the sample prior to digestion, and calculating the extent of digestion from a determination of the "added aneurin" content by the prescribed method. Other disadvantages are the incomplete oxidation of aneurin which occurs when the methyl alcohol, sodium hydroxide and potassium ferricyanide are pre-mixed, and the errors of matching the fluorescence visually. The following procedure avoids these difficulties:—The hand-picked and cleaned sample (1 to 2 lb.) is milled finely in a disintegrating mill, and the resulting flour is assayed within 3 days. To two 20-g. portions are added, respectively, 80 ml. of a 0·1 per cent. solution of pepsin in 0·33 per cent. hydrochloric acid; and 79 ml. of the above pepsin-acid solution and 1 ml. of a standard solution containing 100μ g. of aneurin. After incubation overnight at 37° C., followed by the addition of 2·6 ml. of *N* sodium hydroxide solution and 100 mg. of taka-diastase, incubation is resumed for 5 hours, portions of each mixture being then centrifuged. To 4 alkali-resistant test-tubes (6 × 1 in.) are added the following:—To Nos. 1 and 2, 2 ml. of the clear centrifuged liquid containing no added aneurin; to No. 3, 2 ml. of the centrifugate containing the added aneurin; to No. 4, a mixture of 1 ml. each of the standard solution of aneurin and of water. To each tube is then added 2 ml. of methyl alcohol, followed by 0·2 ml. of water and 1 ml. of 30 per cent. sodium hydroxide solution to tube 1, and by 1 ml. of the alkali and 0·2 ml. of a fresh 5 per cent. solution of potassium ferricyanide to tubes Nos. 2, 3 and 4. A stream of nitrogen is passed through the tubes during, and for 1 minute after, these additions, and also for 3 minutes after the subsequent addition (to each) of 25 ml. of redistilled *iso*butanol which has been saturated with water. The *iso*butanol layers are then filtered through papers which have previously been extracted for 24 hours with the hot (wet) solvent; the filtrates should not be stored in corked vessels, as fluorescent material may be extracted. The fluorescence is measured in a Hills-Cohen fluorimeter (*Biochem. J.*, 1939, **33**, 1966), illumination being provided by a 500-watt mercury arc, which is fitted with two 3-mm. Wood's glass filters separated by a gap of 0·25 inch (which serves as a heat-filter). The fluorescence is measured with a Weston Type "Photronic" cell, fitted with Wratten 2A and 49A filters, and connected to a "Cambridge" short-period galvanometer (resistance, 200Ω). The solutions are matched in "cells," *i.e.* thin-walled specimen tubes (2 × 1 in.) which have no appreciable fluorescence, and the lamp should be standardised between readings against a piece of fluorspar, which is preferable to a solution of quinine sulphate for this purpose, being more stable. The following readings are made:—(1), Cell No. (1) alone; (2), cell (1) containing 15 ml. of unoxidised extract from tube 1; (3), a second cell, No. (2), alone; (4), cell (2) containing 15 ml. of oxidised extract from tube 2; (5), mixture (4) after addition of 0·15 ml. of oxidised extract from tube 4; (6), cell (5) after a second addition of 0·15 ml. of extract from tube 4; (7), a third cell, No. (3), alone; (8), cell (3) containing 15 ml. of extract from tube 3. The difference values (2) − (1), (4) − (3), (5) − (3), (6) − (3) and (8) − (7) enable the extent of digestion to be calculated and allowed for, and a worked example is given in the original paper. Since the extraction of thiochrome by *iso*butanol is incomplete, it is important to adhere to the specified conditions so far as possible, so as to maintain a constant partition-coefficient, and in the event of any variations in the quantities taken (*e.g.* the use of larger aliquot portions owing to the low aneurin-content of a foodstuff) the others must be correspondingly adjusted. When such circumstances necessitate the use of a larger quantity of ferricyanide errors may be introduced, owing to the higher unoxidised blank and the reduction by the ferricyanide of the "blank" fluorescence of the oxidised solutions. If a foodstuff is known to contain no protein-bound aneurin or phosphorylated cocarboxylase (*e.g.* wholemeal flour), the pre-treatment with pepsin or taka-diastase, respectively, may be omitted, and 0·33 per cent. hydrochloric acid used for the extraction, so long as this procedure does not substantially increase the fluorescence of the blank. The standard deviation for 9 separate assays of the same flour (ranging from 2·05 to 2·25μ g. of aneurin per aliquot taken) was 0·081 (*i.e.* approximately 4 per cent. of the mean), and since the fluorescence of the blank rarely exceeds 15 per cent. of that of the oxidised sample and it is unlikely that more than a small fraction of the former is destroyed by oxidation, the accuracy obtainable compares very favourably with that of most biological methods. The aneurin contents of the 78 wheats examined, which represented most available commercial types, were (excluding those of the *Triticum durum* species) 0·54 to 2·60 (average, 1·25); *T. durum* wheats (5 samples), 1·65 to 3·33 (average 2·37); English wheats (33 samples), 0·78 to 1·98 (average, 1·39), I.U. per g. With the exception of *T. durum* the aneurin content bears no consistent relationship to the species, and manuring, soil, climatic conditions or the growing period of the plant fail to explain the variations found; no serious loss of aneurin from wheat occurs after 10 years' storage. The exceptional nature of *T. durum* is evident, even with wheats of this species grown in England, and it indicates that this is a real species difference, which is independent of soil or climate and is possibly related to the fact that the chromosome number of this species differs from that of *T. vulgare*.

J. G.

Bacteriological

Classification and Identification of Bacteria with Special Reference to the Beer Types. J. L. Shimwell. (*J. Inst. Brewing*, 1940, 207–215.)—General principles of classification are discussed, and the criteria available for classification (morphology, motility, orientation, spore formation, cultural characters, physiology, habitat, serological tests, and Gram staining) are reviewed and their limitations pointed out. A proposed key is set out for the determination of the genus of known brewery bacteria, advantage being taken of the fact that only a limited variety of genera occur in that industry. The key is as follows:

1. GRAM POSITIVE.
   - A. *Catalase positive.*
     - (*a*) Rods (1) Form spores. Genus: *Clostridium.*
       (2) Do not form spores. Genus: *Propioni bacterium.*
     - (*b*) Cocci (1) Form cubical packets. Genus: *Sarcina.*
       (2) Do not form cubical packets. Genus: *Micrococcus.*
   - B. *Catalase negative.*
     - (*a*) Rods (1) Form spores, strictly anaerobic. Genus: *Clostridium.*
       (2) Do not form spores, facultative. Genus: *Lactobacillus.*
       Species: *L. pastoranum* (and probably many others not yet recorded).
     - (*b*) Cocci (1) Genus: *Streptococcus.*
       Species: *S. damnosus* (Claussen)
       ,, var. *perniciosus.*
       ,, var. *viscosus.*
       S. tetragenus (Walters).
2. GRAM NEGATIVE.
   - A. *Produce acetic acid from alcohol.*—Genus: *Aceto-bacter.*
     Species: *A. aceti, A. pastorianum, A. viscosum, A. capsulatum,* etc., etc.
   - B. *Do not produce acetic acid from alcohol.*
     - (*a*) Motile.
       (1) With peritrichous flagella: Family *Enterobacteriaceae* ["coliform" types, "wort bacteria"].
       (2) With tophotrichous flagella, produce alcoholic fermentation of glucose.
       Species: *A. anaerobicum.*
     - (*b*) Non-motile, large rods.
       (1) Highly pleomorphic on solid media or in neutral liquid media.
       Species: *Flavobacterium proteus* [the common short fat rod of brewers' yeast].
       (2) Not markedly pleomorphic; produce acetylmethylcarbinol.
       Genus: *Aerobacter.*

When using this key it must be borne in mind that it is purely provisional, and as time goes on and our knowledge of organisms increases it will have to be amplified to include new types and species. Three plates illustrate *Str. damnosus*, a *micrococcus* species, a *sarcina* species, *L. pastorianus*, *Achromobacter anaerobicum* showing flagella, rosette and club-shaped arrangement, rod forms from pitching yeast and a gelatin streak culture of *L. pastorianus*. D. R. W.

Routine Determination of the Bacterial Content of Paper-board. L. C. Cartwright and S. S. Epstein. (*Paper Trade J.*, 1940, **111**, *T.A.P.P.I.Sect.*, 49–51.)—Existing and pending regulations concerning bacteriological standards for paper-board for food containers used in the United States render necessary routine tests of the following nature:—At least 5 reels are sampled, sheets approximately 10 in. square being taken from 5 layers down and trimmed and cut up under aseptic conditions. Ten g. are weighed and put in a sterile Pyrex flask containing 1 litre of sterile water, and the flask is then plugged with cotton wool and maintained at 35° to 40° C. for 2 to 6 hours. Pulping takes place in a welded, stainless steel churn fitted with a twin-propeller electric mixer; a small hole in the cover serves for the withdrawal (in a sterile pipette) of aliquot portions of the pulped sample, without stopping the mixer or exposing the contents of the churn to contamination. Before use the churn, cover and propellers should be wrapped in paper and sterilised at 15 lb. per sq. in. for 30 minutes, the fixed portions which project inside the churn being wiped with 95 per cent. alcohol and "flamed." In routine work with samples of low bacterial content, steam-sterilisation between each pulping operation is unnecessary, the churn being rinsed with 3 litres of sterile water and the propellers and cover washed in alcohol and "flamed." The course of pulping (which takes 20 to 30 minutes) is followed by withdrawing samples in a sterile 10-ml. pipette, the end of which has been cut off and ground to an internal diameter of approximately 4 mm. This sample is transferred from the pipette to a sterile Petri dish (diameter 100 mm.), a nutrient agar medium being then added and the mixture incubated at 37° C. for 48 hours. Three methods of plating with different proportions of medium are compared statistically, and it is concluded

that there is much less chance of the formation of "spreader"-colonies if the strength of the medium is double the normal value. Thus, ten 5-ml. portions of sample were mixed with 5·5 to 6·5 ml. of a medium containing 0·5, 0·3 and 1·5 per cent. of peptone, beef extract and agar-agar, respectively. If an average of the counts obtained for the 10 plates is taken, the result is more reliable than that obtained by plating the equivalent of 0·1 g. of sample into a single large dish. The bacterial counts recorded for a large number of paper-boards vary from 12 to 273 per g. of sample. J. G.

Formation of Trimethylene Glycol from Glycerol by *Aerobacter*. M. N. Nickelson and C. H. Werkman. (*Enzymologia*, 1940, **8**, 252–256.)—The fermentation of glycerol by four strains of *Aerobacter* in a medium of only glycerol and inorganic salts has been found to convert about 45 per cent. of the glycerol into trimethylene glycol. Small amounts of acetyl methyl carbinol and considerable amounts of 2,3-butylene glycol were also found, but no succinic acid. Braak did not observe the formation of trimethylene glycol with two strains of *Aerobacter aerogenes*, but obtained it under anaerobic conditions with a strain which he named *B. Freundii*. With other strains he found that the fermentation of glycerol was at first vigorous, but was later arrested unless a hydrogen acceptor, such as peptone, was present. The paper sets out in tabular form the percentages of biological products of the author's strains and of Braak's strains in a medium of glycerol and inorganic salts. These include hydrogen, carbon dioxide, formic acid, acetic acid, lactic acid, succinic acid, ethyl alcohol, 2,3-butylene glycol, and trimethylene glycol. Experimental methods are described. D. R. W.

Agricultural

Minimum Lethal Dose of Selenium as Sodium Selenite for Horses, Mules, Cattle and Swine. W. T. Miller and K. T. Williams. (*J. Agric. Res.*, 1940, **60**, 163–173.)—Selenium in the form of sodium selenite was given in single large doses to horses, mules, cattle and swine, the dose being calculated as mg. of selenium per pound body weight. The quantity was reduced for other animals until the minimum lethal dose was reached. Five horses and 3 mules were used, and the minimum dose for them was about 1·5 mg. per lb. of body weight. For cattle (one calf 5 days old, 2 cows 3 to 4 years and 2 older) the dose was between 4·5 and 5 mg. per lb. of body weight. For swine (7 of 4 to 6 months) the dose was between 6 and 8 mg. per lb. of body weight. The dose varied considerably for the mules, two of which were fat and one was lean, and it seems probable that, at any rate for horses and mules, animals in good condition may be more susceptible to the action of selenium than thin ones. It may be that if the dose were calculated in terms of blood-volume, rather than for body-weight, the difference would not be so pronounced. D. G. H.

Arsenic in Soils and Waters in the Waiotapu Valley, New Zealand. R. E. R. Grimmett and I. G. McIntosh. (*New Zealand J. Sci. and Techn.*, 1939, **21**, 137–160A.)—Sickness and death of cattle, especially dairy cows, on drained swamp land at Reporoa, in the central volcanic plateau of the North Island, have been found to be associated with high arsenic content in soils and waters. The Waiotapu River frequently floods the low-lying parts of the district, leaving a deposit of arsenical mud in the paddocks, and this appears to be largely responsible for the contamination. In one area the draining of the surrounding land caused the activity of hot springs to cease, but in a rain-fed drinking pool in this area there was a crust, about 1 inch thick, of orange-yellow material composed of silica in admixture with about 5 per cent. of orpiment and realgar. Muds from drains and seepage areas in other parts of the district contained arsenic in amounts up to more than 1 per cent. On one farm a spring with a flow of about 1 gall. per minute contained 2·6 grains of arsenic (as As_2O_3) per gall. Samples taken from under the surface of the Waiotapu River at different points showed various amounts of arsenic up to 0·276 per cent., whilst in the topsoils the amount ranged from 0·525 per cent. downwards. The arsenic on the farm lands was found to be in three forms of chemical combination—acid-insoluble, acid-soluble, and water-soluble, the first corresponding with arsenic sulphide and the second with a compound of arsenic with iron. It is pointed out that the area concerned is relatively small, covering about 2000 acres, and is in a thermal district in which the circumstances are very exceptional.

Chemical Effect on Lead Arsenate of Certain Salts which may be present in Soil and Spray Waters. J. M. Ginsburg, (*J. Agric. Res.*, 1940, **60**, 199–205.)—To investigate the possibility of soluble arsenic compounds finding their way to the roots of trees or crops where arsenical sprays have been used, some 50 salts generally present in soils or spray waters were tested to find to what extent they could give rise to soluble arsenic when in contact with acid lead arsenate used in the strength of 3 lbs. per 100 gallons of water. This solution was left for 24 hours, with frequent shaking, in contact with various concentrations of the salts. Nitrates, sulphates and acetates proved relatively non-reactive; chlorides, silicates and bicarbonates produced moderate quantities, and salts of carbonates and sulphides large amounts of soluble arsenic. The three phosphates of calcium and monobasic phosphates of sodium and potassium formed inappreciable quantities of soluble arsenic, but the dibasic, and particularly the tribasic phosphates of sodium and potassium produced large amounts. Of a group of salts possessing the property of decomposing lead arsenate, the most highly soluble will form more soluble arsenic than the slightly soluble. Salts with *p*H values 8 to

11·4 produced, with the two exceptions of sodium and calcium sulphates, more soluble arsenic than salts with lower *p*H values.
D. G. H.

Manganese Method for Determination of Base Exchange Capacity of Soils and other Materials. C. A. Bower and E. Truog. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 411–413.)—The material is saturated with bivalent manganese by treatment with manganese chloride solution; after displacement, the manganese is determined colorimetrically as permanganic acid. The base exchange capacity of a range of materials tested, *viz.* loams, peat, clays, Bentonite and an artificial zeolite, expressed in milli-equivalents of base per 100 g. of material, was found to be closely similar for manganese and calcium. A 1-g. sample in a 100-ml. stoppered centrifuge tube is shaken vigorously for 5 minutes with 50 ml. of *N* manganous chloride solution. The sides of the tube are washed down with neutral alcohol, and the liquid is centrifuged and poured off. The process is repeated 5 times, which is sufficient to saturate the material with manganese. The excess of manganese chloride is washed out of the material by repeated shaking and centrifuging with 50-ml. portions of neutral 95 per cent. ethyl or methyl alcohol until the washings are free from chloride; 4 washings usually suffice. The exchangeable manganese in the material is now displaced by washing with 5 successive portions of *N* ammonium acetate solution, shaking and centrifuging being used. The washings are combined, and an aliquot portion, containing 0·25 to 0·75 mg. of manganese, is evaporated to dryness. The carbonaceous matter in the residue is destroyed by evaporation with nitric acid. The dry residue is treated with 5 ml. of conc. sulphuric acid, and diluted with about 15 ml. of water; 0·2 g. of sodium periodate is added, and the solution is boiled gently until the colour of permanganic acid appears. The solution is diluted to 90 ml. and kept at 85° to 90° C. for 30 minutes to complete the oxidation of the manganese, after which the solution is cooled, and the manganese is determined colorimetrically.
S. G. C.

Organic

Behaviour of Certain Substituted Allenes towards the Meinel Colour Test. F. B. LaForge and F. Acree, Jr. (*J. Amer. Chem. Soc.*, 1940, **62**, 1621–1622.)—Meinel's test (*Ber.*, 1937, **70B**, 429) for conjugated double bonds is based upon the treatment of the compound with one molecular equivalent of bromine in methanol solution. The isolated methyl hypobromite addition product is treated with a suspension of silver thiocyanate containing ammonium ferric sulphate. The formation of a red colour was stated to indicate the presence of a conjugated system of double bonds. In the authors' experiments on the reaction of halogens with compounds having a cumulated system of double bonds it was found that 1-phenyl-1.2-butadiene, 2.3-pentadiene, 1-cyclohexyl-2.3-pentadiene and pyrethrone gave a positive Meinel reaction. When compared with myrcene, 1-pentene and styrene dibromide the approximate speed and the intensity of colour were greatest with 1-phenyl-1.2-butadiene and decreased in the order named with the other compounds. As compounds possessing a cumulated system of double bonds also respond to the Meinel test, the method is not specific for the conjugated system.
E. M. P.

Analysis of Rosin Size. E. A. Georgi. (*Paper Trade J.*, 1940, **111**, *T.A.P.P.I. Sect.*, 83–84.)—For the determination of free rosin in rosin size, extraction (*e.g.* with absolute or 95 per cent. alcohol) followed by titration of the extract with a standard solution of potassium hydroxide in alcohol is usually advocated. Objections to this are the hydrolysis of saponified rosin, which also contributes to the titration; the extraction of carbonates and bicarbonates; and the difficulty of titrating the highly-coloured extract obtained. The method now suggested is adapted from that used for the titration of wines, and it may also prove suitable for use with other dark-coloured liquids. It depends on the fact that the use of a filter having the same transmission-band as the absorption band of the indicator in its alkaline state, results in the transition from a bright to a dark field at the end-point. The sample therefore, is dissolved in alcohol in a beaker, which is supported over an Eastman's Wratten Filter 52, below which is a heat-absorbing (*e.g.* Corning Aklo) filter, and under the latter an electric light. Titration is then carried out with thymol blue as indicator, the end-point being a change in the intensity of the transmitted light instead of a change in colour. A change in colour may, however, also sometimes be observed because different samples of size vary in their powers of transmission. Free alkali in size is best determined by dissolving 5 to 7 g. of the sample in a beaker in 35 ml. of neutral anhydrous *iso*propyl alcohol, the alcohol being added a drop at a time at first, with continual stirring, so as to avoid the formation of lumps. An additional 15 ml. of the alcohol are finally added, the beaker is placed in an air-tight container for 4 hours, and the mixture then filtered through a No. 40 Whatman paper (11 to 12·5 cm.), the residue being washed with hot neutral *iso*propyl alcohol until free from size. The filter-paper is washed with 100 ml. of water (free from carbon dioxide), and the new filtrate is titrated in the usual way with 0·1 *N* hydrochloric acid, with phenolphthalein and methyl orange as indicators.
J. G.

Studies in the Composition of Coal: Extraction of Coal with Quinoline. R. Belcher and R. V. Wheeler. (*J. Chem. Soc.*, 1940, 866–869.)—Suggestions have previously been made (*e.g.* by Vignon, *Compt. rend.*, 1914, **158**, 1421) to use quinoline instead of pyridine for the primary extraction of coal in the

determination of resins and hydrocarbons. The present experiments showed that extraction with quinoline is slower than with pyridine and is no more complete. In addition, technical quinoline undergoes a photochemical synthesis on heating, presumably reacting with some of its impurities, and the results may therefore be erroneous. E. M. P.

Unsaponifiable Matter in Sulphated Oils and Fatty Alcohols. Committee on Oils, Fats and Waxes. No. XIII. Part I. D. Burton and G. F. Robertshaw. (*J. Int. Soc. Leather Trades' Chem.*, 1940, **24**, 293–298.)—It is generally assumed that the unsaponifiable matter in sulphated oils and fatty alcohols is present before sulphation, or has been added after sulphation, and this may lead to mistaken ideas concerning the composition of some sulphated compounds. Thus, higher fatty alcohols or insoluble organic bases may be present as sulphuric esters (which produce special emulsifying properties), or in combination with carboxylic acids or sulphonic compounds, and determination of the saponifiable matter by saponification with 0·5 *N* alcoholic potassium hydroxide solution will not decompose these (unless, possibly, the oil has a high water-content). If, however, the oil is first split (*e.g.* with *N* sulphuric acid) and then saponified, these higher fatty alcohols and insoluble organic bases will be included in the unsaponifiable matter; this method has proved useful for sulphated sperm oil and sulphated fatty alcohols. The method recommended in the S.P.A. Report No. 1 of the Analytical Methods Committee on Determination of Unsaponifiable Matter in Oils and Fats (ANALYST, **1933**, **58**, 203) should be used for oils which are saponified only with difficulty, and contain unsaponifiable matter which is not easily extracted completely with petroleum spirit (*e.g.* sulphated fish, shark and sperm oils); however, although the ethyl ether recommended for extraction removes a wider range of water-soluble substances than petroleum spirit, it has the disadvantage that it also extracts more soap. With one sulphated product made from a raw material containing higher fatty alcohols or their esters it was found that 7 per cent. of the 35 per cent. of unsaponifiable matter was not recovered until the oil had been split with *N* sulphuric acid (Hart's method), and that, even after splitting, 3 per cent. was still not recovered. The procedure was to remove the alcohol, by evaporation, from the saponified soap solution, which was then neutralised to methyl orange with *N* sulphuric acid and boiled for 2 hours with an additional 50 ml. of *N* sulphuric acid; the fatty matter which separated was then extracted with ethyl ether, and a subsequent test showed it to be free from sulphur. These results may be explained by the formation of sulphuric esters from the unsaturated or hydroxyl groups (or both) present in the higher fatty alcohol esters. In the determination of the unsaponifiable matter the sulphated product is saponified, but the sulphuric ester groups remain intact, and the free alcohols (but not the fatty alcohol sulphuric esters) are extracted by the ether. During the splitting process, however, the alcohols present as sulphuric esters are liberated and are extracted by the ether, although not necessarily completely. The Schindler fractionation method cannot be used for the accurate determination of the unsaponifiable matter in a sulphated oil, partly because of the difficulty of ensuring complete fractionation and partly because decomposition of the sulphuric esters may occur during fractionation. It is therefore suggested that the normal procedure should be followed to the point at which a solution of the β-fraction in alcohol and of α_1- and α_2-fractions in petroleum spirit are obtained. The unsaponifiable matter is then determined in the latter by evaporating the solution and applying the S.P.A. method (*loc. cit.*); in the former by neutralising the acetic acid with potassium hydroxide, evaporating to remove the water and alcohol, and after adding 25 ml. of 0·5 *N* alcoholic potassium hydroxide solution, following the S.P.A. method. A solution, in 50 ml. of water, of the residue obtained after evaporation of the soap solution is boiled for 1 hour with 26 ml. of 0·5 *N* hydrochloric acid and 5 g. of sulphuric acid in order to split the sulphuric esters, and the resulting solution is extracted with ether. The ethereal extract is washed with water until free from acid and then evaporated, and the unsaponifiable matter in the residue is determined by the S.P.A. method. The unsaponifiable matters obtained from a sulphated sperm oil were:—α_1- and α_2-fractions, 16·7; β-fraction, 4·1; present as sulphuric ester, 13·7; total, 34·5 per cent. The unsaponifiable matter, as determined after splitting with *N* sulphuric acid in the determination of combined SO_3 (Hart's method) was 36·7 per cent., and the difference between this and 34·5 per cent. is mainly accounted for by the presence of unsaponifiable matter in the γ- and δ-fractions, which was not determined. The Wizoeff method for this determination, in which the sulphuric acid ester group is removed before the determination of the unsaponifiable matter, is regarded as inaccurate, because the result includes free unsaponifiable matter plus unsaponifiable matter present in combination in sulphuric esters. J. G.

Oxidation of Drying Oils and Cognate Substances. VI. Properties of the Peroxide, Ketol and Oxido Groupings, including those of some Resins. R. S. Morrell and E. O. Phillips. (*J. Soc. Chem. Ind.*, 1940, **59**, 144–148T; *cf. ibid.*, 1939, **58**, 159T.)—In continuation of the investigation of the oxidation of drying oils and some resins, the action of hydrogen iodide on substances containing contiguous hydroxyl groups was examined. With polyhydric alcohols the action is variable; with hydrobenzoin, normal; with glycerol, negligible; with ethylene glycol, partial interaction occurs; with dihydroxy acids, the cis-form reacts the more strongly. A study of the

reactive oxygen values of rosin indicated that nearly 75 per cent. of the calculated polymerised peroxide was formed, and a rosin ester film on drying in air behaves as a drying oil as far as oxidation is concerned. In blonde shellac the R.O. value was found to be 3·31, and a ketone grouping is indicated. A study of enolisation of the ketone grouping has been made, and the discrepancy between the iodine values obtained by the Hübl method (10·2) and Wijs method (87·2) is due to this, the isomeric ketol acids showing 64–99 per cent. enolisation. Whenever a ketol group is present the iodine value will be variable, and its magnitude will depend on the solvent, the temperature, and the symmetry of the molecule. The oxido grouping in oxidoelaidic acid was studied. It is not reduced by hydrogen, forms a hydrobromide, and polymerises at 100° C. to a dimeride. The investigation of the methylation products of oxidised β-elaeostearin has been continued, and earlier results of Morrell and Marks (*J. Soc. Chem. Ind.*, **1931, 50**, 27T) have in general been confirmed, with some modifications due to the application of the R.O. values. The esterified product was separated into fractions insoluble and soluble in petroleum spirit, and structural formulae were assigned to them. The reduction of the methyl oxido-methoxy β-elaeostearic acid by hydrogen at atmospheric pressure with a platinum catalyst was unsuccessful as regards the oxido group owing to the very slight fall in R.O. value, accounted for by partial reduction of the methylated ketone grouping. D. G. H.

Effect of Ferric Sulphate in Shortening the Digestion Period in the Kjeldahl Method. F. M. Stubblefield and E. E. Deturk. (*Ind. Eng. Chem., Anal. Ed.*, **1940, 12**, 396–399.)—The use of the following mixture is claimed to give more rapid digestion than the normal Kjeldahl–Gunning–Arnold process: 25 ml. of conc. sulphuric acid, 0·6 g. of metallic mercury, 10 g. of anhydrous dipotassium phosphate and 6 g. of ferric sulphate.

S. G. C.

Inorganic

Determination of Sodium in Presence of Other Metals. E. C. Elliott. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 416–417.)—The method of Caley and Sickman (*J. Amer. Chem. Soc.*, 1930, **52**, 4247) employing precipitation with magnesium uranyl acetate reagent, was used. It was confirmed that small amounts of sodium can be determined without interference in presence of beryllium, cerium, lanthanum, neodymium, thallium, thorium, vanadium and zirconium. Silica, if present, should be removed by evaporation with hydrofluoric acid and a little sulphuric acid. Tantalum and niobium form gelatinous precipitates with the reagent and must be separated prior to determination of sodium. S. G. C.

The Fischer Volumetric Method for the Determination of Water. E. G. Almy, W. C. Griffin and S. C. Wilcox. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 392–396.)—The Fischer method (*Z. Angew. Chem.*, 1935, **48**, 394) consists in titrating the sample with a solution containing methanol, iodine, sulphur dioxide and pyridine; the colour of free iodine appears when all the water has been titrated, indicating the end-point. The present authors propose a potentiometric method for the detection of the end-point to render the process applicable to dark coloured solutions. The titration vessel consists of a flask fitted with a four-holed bakelite stopper accommodating (*a*) burette nozzle, (*b*) stem of a paddle for mechanical agitation during titration, (*c*) platinum wire electrode, and (*d*) tungsten wire electrode. A thermionic valve type millivoltmeter is required for detection of the potential changes of the electrodes. The reagent is prepared by mixing 203 g. of liquid sulphur dioxide with each 1 kg. of pyridine; to 1359 g. of this mixture, after cooling, are added 1786 g. of methanol followed by 454 g. of iodine, with efficient cooling; the reagent is allowed to "age" for a few days before use. *Method.*—The sample, containing 0·05 to 0·2 g. of water, is mixed with a measured excess of reagent in the titration flask. The liquid is then back-titrated with a solution of water in methanol (5 g. per litre) in order to determine the residual excess of reagent. The end-point is shown by a sudden rise in E.M.F. of the platinum-tungsten couple. A second titration is made to determine the equivalence of the reagent and the alcoholic water solution. The ultimate standardisation of the reagent is carried out by adding a weighed quantity of water to an excess of the reagent and back-titrating with the alcoholic water solution; daily standardisation of the reagent is recommended, owing to a slow change in its water-equivalent. The method is applicable to numerous substances: oils, fats, waxes, monohydric and polyhydric alcohols, glue; insoluble powders may be treated after vigorous agitation with the reagent or prior suspension in anhydrous solvent. Substances which react rapidly with free iodine cannot be dealt with, but if the reaction with iodine is slow a good approximation to the water content can be obtained by carrying out the method rapidly. Inorganic hydroxides interfere by reacting with acids formed in the titration, yielding a salt and water. Acids which react with methanol, liberating water, also interfere, boric acid for example; acetic acid, however, does not interfere, and water in glacial acetic acid may therefore be determined. The nature of the reaction of water with the reagent is obscure (*cf.* Smith, Bryant and Mitchell, *J. Amer. Chem. Soc.*, 1939, **61**, 2407). S. G. C.

Modification of the J. Lawrence Smith Method for the Extraction of Alkalis in Rocks. R. E. Stevens. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 413–415.)—Barium chloride (1 g.) is substituted for the ammonium

chloride (0·5 g.) customarily used in the sintering mixture. The details of the process are similar to those of the usual J. Lawrence Smith process. The advantages claimed are the elimination of the preliminary slow heating of the charge to remove ammonia, saving about ¾ hour, and the automatic removal of sulphate.

S. G. C.

Microchemical

Micro-determination of Bromine in Foodstuffs. W. P. Ford, D. W. Kent-Jones, A. M. Maiden and R. C. Spalding. (*J. Soc. Chem. Ind.*, 1940, **59**, 177–180T.)—Methods for the determination of bromine in foodstuffs must take into account the presence of relatively large quantities of chlorides, and they fall into 3 categories:—(*a*) The use of a colorimetric reagent, which reacts with bromine but not with chlorine (*cf.* Seaber, ANALYST, 1936, **61**, 14). (*b*) The preferential liberation of bromine by controlled oxidation (*cf.* Francis and Harvey, *Biochem. J.*, 1933, **27**, 1545); this is the most direct method, although its accuracy depends on a balance of errors due to the loss of some bromine and the liberation of chlorine (*cf.* Hahn, *Mikrochem.*, 1933, **17**, 222). The present authors obtained recoveries of bromine of 85 to 110 per cent. from flour which had been treated with potassium bromate equivalent to 6 parts of bromine per million; this is regarded as satisfactory. (*c*) Oxidation of bromides to bromate by hypochlorous acid, followed by liberation of iodine from an iodide in acid solution (*cf.* Kolthoff and Yutzy, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 75). Advantages are that the accuracy is unaffected by chlorides, and that 1 bromide ion is equivalent to 6 iodine atoms; disadvantages are the large blank correction often involved and the possibility of the formation of chlorates during oxidation. Since the colorimetric method (*a*) has with very few exceptions hitherto been used for foodstuffs, determinations were carried out by method (*b*) and a combination of a "protected" ashing process and method (*c*). When the bromine-content is such that a quantity of sample containing 0·5 g. of dry solids can be used for the determination, the sample is evaporated with 2·5 ml. of 10 per cent. potassium hydroxide solution in a nickel crucible, and the residue is ignited for 40 minutes at 480° to 500° C.; the ash is then moistened with 1·5 ml. of water and dried, and the ignition process is repeated for 20 minutes. If the bromine-content is lower, 2·5 g. of dry solids and 5 ml. of the alkali are used, the crucible being placed in a cold muffle furnace and heated to 300° C. in 30 minutes; the contents are then stirred, and the temperature is raised to 500° C. in 40 minutes. After cooling, addition of 10 ml. of water and drying, ignition is completed at 480° to 500° C. for 1 hour, and the ash is extracted once with 15 ml. and twice with 10 ml. of warm water. The residue from the filtration, together with the filter-paper, are dried with 1 ml. of the alkali and ignited for 45 minutes at 480° to 500° C., the extraction process described above being repeated. Finally, the filtrates are combined and evaporated, and the residues are ignited for 20 minutes at 480° to 500° C. The details given above are important if losses of bromine are to be avoided. In method (*c*) the ash is extracted 3 times with 0·75 ml. of water "and" (plus?) 20 ml. of alcohol, the alcohol being removed from the combined filtered extracts by placing the flask containing them in a boiling water-bath and sucking air through it. The solution is then heated in a boiling water-bath for 10 minutes under a reflux condenser with 5 ml. of 15 per cent. sodium chloride and 0·75 ml. of 15 per cent. potassium dihydrogen phosphate solutions, and 0·25 ml. of a solution prepared by absorbing 7 g. of chlorine in a solution of 12 g. of potassium hydroxide in 100 ml. of water. Five ml. of water and 1 ml. of 10 per cent. sodium formate solution are added, and the heating is resumed for 10 minutes, the sides of the condenser being again washed down with 5 ml. of water after 5 minutes. The solution is cooled to 22° C. and allowed to stand in the dark with 1 ml. each of 10 per cent. potassium iodide solution, 2·5 per cent. ammonium molybdate solution, and 1·25 ml. of 4 *N* sulphuric acid. It is then titrated with 0·001 *N* sodium thiosulphate solution until pale yellow, 1 ml. of a 2 per cent. solution of Lintner soluble starch being added, and the mixture diluted to 50 ml. in a Nessler cylinder. The titration is completed, comparison being made with a cylinder containing the solution from a titration which had been completed a few minutes previously and kept in the dark in the interval. With a correction for a blank titration, recoveries of bromine of 85 to 106 per cent. from various foodstuffs (and of 97 to 99 per cent. from 60μ g. of potassium bromide) are obtainable, and only insignificant amounts of chlorate are formed. The necessity for the use of ammonium molybdate to catalyse the reaction between the bromate and iodide ions arises from the fact that the sodium formate used to reduce the excess of hypochlorous acid retards the former reaction. Traces of copper markedly catalyse oxidation of the iodide ion by air, and should be avoided. Any iodine present in the sample also figures in the result, but a study of the literature shows that with normal foods this amounts to only about 2 per cent. of the figures now recorded for the bromine-contents. These results show that the 32 samples of common foodstuffs examined (untreated wheat flour, white and wholemeal breads, tap water, meat, milk, salt, yeast and potatoes) contained 1 to 17 p.p.m. of bromine, and they confirm those of previous workers (which are also tabulated); dried rat's brains contained 23, and dried rat's liver 19 p.p.m. The two methods gave results agreeing well with method (*c*), being checked in an independent laboratory. Wheat flours guaranteed to be free from chemical treatment contained 2·4 to 7·7, and white breads 1·6 to 5·4 p.p.m. "Treatment" of flour with potassium bromate containing bromine equivalent to 3·6 p.p.m.

raised the bromine-content of the bread by only about 2·5 p.p.m., so that it is not possible to ascertain from the bromine-content if a flour has been so treated. J. G.

Microchemical Determination of the Reducing Power of Cellulose, Oxycellulose and Hydrocellulose (Micro-Copper, Micro-Ferricyanide and Micro-Iodine Numbers). E. Geiger and G. Müller. (*Helv. Chim. Acta*, 1940, **23**, 820–826.)—The relative merits of the 3 determinations are compared, and the results obtained on the macro-scale with rayon and oxycellulose (oxidised rayon) are tabulated. The values found, respectively, were:—Copper number, 12·4, 54; iodine value, 10·0, 19·0; ferricyanide number, 56·9, 133·6. The ratios oxycellulose/regenerated cellulose for the 3 methods were, respectively, 4·37, 1·90 and 2·35. The copper number is considered to give the most useful and consistent results, although it is influenced appreciably by the experimental conditions (*e.g.* concentration, alkalinity and quantity of sample used), and these must be observed closely in carrying out the micro-modification of the method. The basis of this is the determination of ferrous iron colorimetrically, instead of by titration with potassium permanganate solution. *Micro-copper number* (*cf.* Knecht and Thompson, *J. Soc. Dyers & Colourists*, 1920, **36**, 255).—The sample (0·1 to 10 mg., corresponding with a copper number of 10 to 0·1 g. of copper per 100 g. of sample) is sealed in a tube (length 3 cm., diameter 2·5 mm.) with 0·04 ml. of Braidy solution (*i.e.* a mixture of 5 ml. of a 10 per cent. solution of crystalline copper sulphate, and 95 ml. of a solution containing 50 g. of sodium carbonate per litre). The tube is immersed for 3 hours in a boiling water-bath, and then cooled and opened, the sample is removed with a fine glass hook and the liquid is filtered in a sintered glass micro-crucible. The residue is washed first with the Braidy carbonate-bicarbonate solution, then with 1 drop of 2 *N* sodium carbonate solution and finally 3 times with 3 drops of cold water. The filtrate is rejected, and the cuprous oxide in the residue is dissolved in 1 drop of a solution containing 5 per cent. of ferric sulphate and 20 per cent. of sulphuric acid; 3 drops of water, 1 drop of 2 *N* sulphuric acid and three 3-drop portions of water are used, in succession, for washing. Then the ferrous salts in the resulting filtrate are determined by adding 3 drops of a 1 per cent. solution of $\alpha.\alpha'$-dipyridyl or (preferably, since it is more sensitive and cheaper) of *o*-phenanthroline hydrochloride, followed by 1 drop of 10 per cent. ammonium acetate solution, a deep red or orange-red colour, respectively, developing in about 10 minutes. Three drops of a 1 per cent. solution of sodium fluoride and sufficient water to bring the total volume to 10 ml. are then added, and the colour is matched against that produced in a similar way from a 0·0152 per cent. solution of ferrous sulphate, which has been standardised with 0·04 *N* potassium permanganate solution, a volume equivalent to 20 to 80γ of ferrous sulphate being diluted to 10 ml. for the purpose; allowance is made for a blank determination. Beer's Law applies for concentrations up to 0·2 mg. per 100 ml., but a calibration curve is necessary with higher concentrations. *Micro-iodine value* (*cf.* Bergmann and Machemer, *Ber.*, 1930, **63**, 316, 2304).—The sample (0·25 to 25 mg. corresponding with an iodine value of 20 to 0·2 ml. of 0·1 *N* iodine solution per g. of sample) is treated for 90 minutes with 1 ml. each of 0·25 *N* sodium hydroxide and 0·005 *N* iodine solutions. The unused iodine is then back-titrated with 0·005 *N* sodium thiosulphate solution in presence of 0·3 ml. of *N* sulphuric acid. *Micro-ferricyanide number* (*cf.* Freiberger *Melliand's Textilber.* 1930, **11**, 127).—The sample (0·5 to 50 mg., corresponding with a ferricyanide number of 200 to 2 g. of potassium ferricyanide per 100 g. of sample) is treated with 1 ml. each of 0·005 *N* potassium ferricyanide and 10 per cent. sodium hydroxide solutions for 10 minutes in a boiling water-bath. The mixture is rapidly cooled, and 0·5 ml. of 30 per cent. acetic acid, 1 ml. of a solution containing 50 g. of zinc sulphate and 10 g. of sodium chloride per litre and a crystal of potassium iodide are added in succession. The unused ferricyanide is then back-titrated with 0·005 *N* sodium thiosulphate solution, allowance being made for a blank determination. Results are tabulated for cotton linters and for viscose rayon alone and containing oxycellulose or hydrocellulose. Slight deviations between duplicate results obtained for the same sample are attributed to sampling errors. The silver nitrate method for the determination of reducing power (*cf.* Götze, *id.*, 1927, **8**, 624, 696) is considered unreliable. J. G.

Thorium Nitrate Micro-titration of Fluorine in Aqueous and Alcoholic Systems. J. W. Hammond and W. H. MacIntire. (*J. Assoc. Off. Agr. Chem.*, 1940, **23**, 398–404.)—A brief review of the difficulties encountered in the determination of small amounts of fluorine by titration with thorium nitrate solutions is given, and also an account of experiments to determine (*a*) the influence of fluorine concentration upon the accuracy of the titration in buffered aqueous and 48 per cent. alcoholic systems and in corresponding systems in which the *p*H is adjusted by means of 0·05 *N* hydrochloric acid; (*b*) the conditions under which the value of the thorium nitrate solution follows the stoichiometric equation, and those under which its value is empirical and determinable only by standardisation against standard fluorine solutions. In this work precautions were taken to prevent coatings of colloidal silica in the distillation flasks and to maintain the distillation temperature at 135° C. Two drops of a 0·05 per cent. aqueous solution of sodium alizarin sulphonate indicator per 10 ml. were used in each titration. The aqueous and alcoholic systems were brought to *p*H 3·0 ± 0·2, and one series of each type was neutralised and

adjusted to that *p*H with 1 ml. of 0·05 *N* hydrochloric acid per 20 ml., and another series of each type was similarly adjusted with 1 ml. of buffer solution containing 9·448 g. of monochloroacetic acid and 2 g. of sodium hydroxide per 100 ml. The thorium nitrate solutions were 0·0175 *N* and 0·00175 *N* for respective titrations of fluorine concentrations of mg.-range and γ-range per 10 ml. The two solutions were standardised against ammonium oxalate and against rock phosphate No. 56 of the Bureau of Standards. The fluorine concentration ranges used were 2 to 50γ per 10 ml. (γ-range) and 0·2 to 5 mg. per 10 to 20 ml. (mg.-range). In alcoholic systems, in the γ-range moderately good agreement was obtained between the acid-adjusted solution and the buffered solution, the buffered solutions giving the higher value, which was also higher than the true value. In aqueous systems, in the γ-range the results in both series of solutions were greatly in excess of the true value, and in the buffered solution again in excess of those in the acid-adjusted solution. In the mg.-range good agreement with the true value was obtained in all the series—aqueous, alcoholic, acid-adjusted and buffered solutions. Blank determinations gave higher results with the buffered solutions in all series in both ranges, and in the γ-range magnified the error in the quantity of fluorine indicated by the titration, particularly in the aqueous system. The results show that micro quantities of fluorine cannot be determined in aqueous systems if the normality value of the thorium nitrate solution is used. For such quantities the value of the solution must be determined empirically against corresponding known quantities of fluorine and for the specific solvent, definite volume, and identical quantity of indicator. When titrations are made in alcoholic solution, however, application of the stoichiometric value of the thorium nitrate solution will give accurate results in a solution of adjusted *p*H without inclusion of a buffer solution. A. O. J.

Photographic Silver-gelatin Paper as a Reagent in Spot Analysis. G. Schwarz. (*Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 369–372.)—Photographic paper developed to complete blackness reflects more brightly after being dipped in hot water. This brightening is prevented by all mercaptans and seleno alcohols, by certain heterocyclic substances containing imino groups, by salts of the nobler metals, by iodides, and by substances which easily split off selenium or tellurium, and the reaction is applied as a spot test for these substances. *Detail.*—Silver chloride or slightly sensitive silver chloride-bromide glossy paper (Velox, Ridax, etc.) is suitable, but any new paper should be tested before use. A suitable paper is fully exposed by artificial light or daylight and fully developed, without exclusion of light, the usual developer and fixing baths and considerable excess of developer being used. The paper is washed for 1 hour in tap water, then in frequent changes of distilled water, and dried and cut into suitable sizes for testing; it will keep indefinitely. To test a reagent paper, a piece is dipped halfway into water at 70°–80° C.; in about 3-5 seconds a very distinct decrease of the blackening must be visible. A small drop of the test solution is placed upon the dry reagent paper and allowed to evaporate or, alternatively, the excess is removed with filter-paper after 5 minutes, but this gives a less sensitive reaction. The strip of paper is then dipped into hot water at 70°–90° C.; the reaction is positive if the spot upon which the drop was placed is black against a gray background. The used paper may be dried and kept as a permanent record. Forty-two organic compounds were tested, and the limits of identification in acid and alkaline media are given. In addition, 14 inorganic compounds were tested. For some substances the test was sensitive to a limiting concentration of 1:100,000. J. W. M.

Reviews

ELECTROCHEMISTRY AND ELECTROCHEMICAL ANALYSIS. VOL. II, GRAVIMETRIC ELECTROLYTIC ANALYSIS AND ELECTROLYTIC MARSH TESTS. By H. J. S. SAND. Pp. ix + 149. London: Blackie & Son, Ltd. Price 5s.

Dr. Sand's name has been for so long associated with electrochemistry and electrochemical analysis that he was the natural choice for the authorship of a modern book, in English, to succeed the classic works of Edgar F. Smith and Classen. The preface to Vol. I announced the completion of the work in a second volume, but it has since been found impossible to include all that was intended, and Potentiometric and Conductimetric Titrations, Moisture determinations by means of capacitance measurement and the electrical measurement of *p*H have been left for the third volume, to be published when circumstances permit.

In this, the second volume, there are chapters on Apparatus for gravimetric electrolytic analysis, Technique of electro-analytical deposition, Quantitative deposition and separation of individual metals, Separations, Application to the analysis of industrial alloys, Internal electrolysis, Electrolytic micro-analysis, and Electrolytic Marsh tests. The use of the auxiliary electrode is described, as are the various measuring devices for the control of cathode potential—an essential to the separation of metals by graded potential. The usefulness of the section on Internal electrolysis, a method which Dr. Sand and his collaborators at the Sir John Cass Institute have done so much to develop during the last decade, is increased by the inclusion of details of a number of actual separations. In the chapter on quantitative deposition and separation of individual metals the gap existing between theory and practice is revealed. Suitable conditions for the deposition of the commoner metals are given in the form of actual examples; indeed, they are referred to as "prescriptions." Complex ion formation, metal overvoltage, initial concentration of the electrolyte, efficiency of stirring, type of electrode, volume of solution, and even the shape of the beaker, are among the factors which control the separations, so that a measure of empiricism is inevitable. In general, examples are given of depositions from various media, *e.g.* silver from nitrate, ammoniacal, cyanide, and acetate solutions.

The section devoted to the separation of metals is not so comprehensive as might have been expected, but there is a chapter dealing with the analysis of yellow metal alloys, white metal alloys, nickel bronzes and aluminium alloys. The section on micro-analysis contains a list of references to original papers: Pregl's method is described, and also Lindsey and Sand's method for micro-deposition under controlled potential. Descriptions of this and many other developments mentioned in the book have already appeared in THE ANALYST.

In the preface, Dr. Sand craves pardon for having given any undue prominence to those developments with which he has been personally associated. This characteristic modesty of the author is, in a sense, reflected in the book. The reviewer would have preferred to see Dr. Sand's life work perpetuated, not in three small pocket books, but in one complete volume which could take its place on the shelf with Treadwell and Sutton and Hillebrand and other classics. Not only would this have done more adequate justice to the author, but it would the more readily have achieved his aim, "to contribute to the more extensive employment of electrolytic methods." It is probably true that these are too seldom used, and while the price of platinum is no doubt an adverse factor, lack of appreciation of the elegance and speed of the methods is also responsible. Dr. Sand's book should go far to remedy this state of affairs, but not so far as it might have gone had there not been a tendency to divide its appeal between the student and the practising analyst.

R. C. CHIRNSIDE

PROPERTIES OF ORDINARY WATER SUBSTANCE. By N. E. DORSEY. Pp. xxiv + 673. New York: The Reinhold Publishing Corporation; London: Chapman & Hall, Ltd. 1940. Price 90s. net.

This monumental compilation of physical data concerning steam, water and the ices having the ordinary isotopic composition was begun under the auspices of a committee of the National Bureau of Standards. In addition to relevant data from the International Critical Tables, revised and supplemented in the light of work published as late as 1937, there is much other information about water, including references to its synthesis and decomposition, but chemical reactions with other substances and solubilities in it of materials other than certain gases are omitted.

Those who occasionally consult the International Critical Tables not infrequently encounter difficulty in determining the precise meaning of the data, but this objection is largely absent from the book under review as a result of the explanations in the tables. It is, however, unfortunate that some device is not uniformly employed to distinguish explanatory matter associated with the tables from the text, which is frequently inserted as a few lines between tables and is then, without notice, continued somewhere on a subsequent page which has to be discovered by trial and error.

Notwithstanding this defect, which could be avoided easily in a future edition, the author is to be congratulated on producing a valuable work of reference.

J. G. A. GRIFFITHS

FORENSIC CHEMISTRY. By H. T. F. RHODES. Pp. viii + 214. London: Chapman & Hall, Ltd. 1940. Price 12s. 6d. net.

This volume is a compilation of information widely diffused throughout criminological literature and a description in brief of the work of a forensic chemical laboratory. Part I deals with personal identification by means of skin prints, occupational dust, blood grouping and seminal stains, and the remainder of the volume gives details of the examination of stains, firearms, documents, inks, paper and subsidiary materials such as sealing wax and adhesives. Methods adopted in the investigation of banknotes and coins are described. The last chapter deals with the isolation and identification of toxic agents, including abortifacients, acids, alkalis, metallic salts, volatile poisons, alkaloids, synthetic drugs and toxic gases. It will thus be evident that much has been crowded into a relatively small space, but the author's excellent literary style has prevented undue compression and sacrifice of lucidity.

The practice of forensic chemistry necessitates the highest degree of accuracy possible, but, unfortunately, much of the subject matter of this volume fails lamentably in this respect. In several instances the only tests given for a particular substance are comprehensive in character and yield the same result with various other compounds, notwithstanding the author's statement on p. 41 that "No test of a general kind can supply precise information."

The different subjects have received very unequal treatment; thus some 12 pages are devoted to the development of skin prints, 6 to the constitution of tannic acid, iron tannates and haematoxylin, and less than 2 to the toxic gas carbon monoxide, since according to the text "this is the only gas which has much forensic importance." To the reviewer the section on "spot" tests for metals appeared curiously familiar, and a brief comparison showed that these had been abstracted almost *in toto*, with slight transposition and without acknowledgment, from a well-known trade publication. Unfortunately during the process a few errors have crept in, whilst the table of micro-reactions for the common metals given on p. 21 perpetuates two errors which occur in the original source and should have been eliminated. Adoption of some of the methods described for the examination of

dusts would lead to the loss of valuable material, and some of the statements relating to this subject are both contradictory and inaccurate.

The section dealing with the isolation of alkaloids and other substances in a pure state from viscera conveys the impression that this is a simple matter, and the smaller details upon which success so largely depends, and which are acquired only by extensive experience, are missing.

The volume concludes with a list of references arranged in alphabetical order of the authors' names, a name index and an accurate, though incomplete, subject index. It is greatly to be regretted that this handbook, which might have been a valuable production, is so seriously marred by errors of various kinds; a thorough revision will be necessary before it can be recommended. T. J. WARD

CHAMBERS'S TECHNICAL DICTIONARY. Edited by C. F. TWEENEY and L. E. C. HUGHES. Pp. viii + 957. London: W. R. Chambers, Ltd. 1940. Price 15s. net.

This dictionary supplies a distinct want, for every science, industry and trade has its words of specialised meaning, many of which have crept into everyday language and are often only imperfectly understood by those who use them. The scope of the work is very wide, for it covers all the pure and applied sciences, medicine and psychoanalysis, construction, including buildings, bridges and ships, all the principal manufacturing industries including raw materials, processes and machinery, crafts and so forth. Authorities in each subject have contributed definitions of terms used in their respective fields, and most of these can be grasped by the layman. The chemical definitions, however, for which Dr. C. J. W. Hooper, Dr. R. G. Israel and Mr. I. Singleton are responsible, are often of the nature of the definitions in a chemical dictionary, since they give structural formulae, melting-points and reactions, and could not be understood by those who have no chemical knowledge. It is difficult, however, to see how a ketone, for instance, could be defined in such a way as to be understood by anyone who knows nothing of organic chemistry; the problem seems insoluble.

A useful feature is the introduction of registered trade names, such as Cellomoid, Pilanco, Maxweld, Pressspahn, which are spelt with capitals to distinguish them from ordinary trade names. The pronunciation of all the words defined is clearly indicated, and the book is printed in clear type, so that there is no difficulty in finding any given entry. It concludes with a classified bibliography of standard works on the principal sciences, industries and trades. The editors, contributors and publishers may be congratulated on the production of a very valuable work, which will be kept in constant use by those who have it. EDITOR