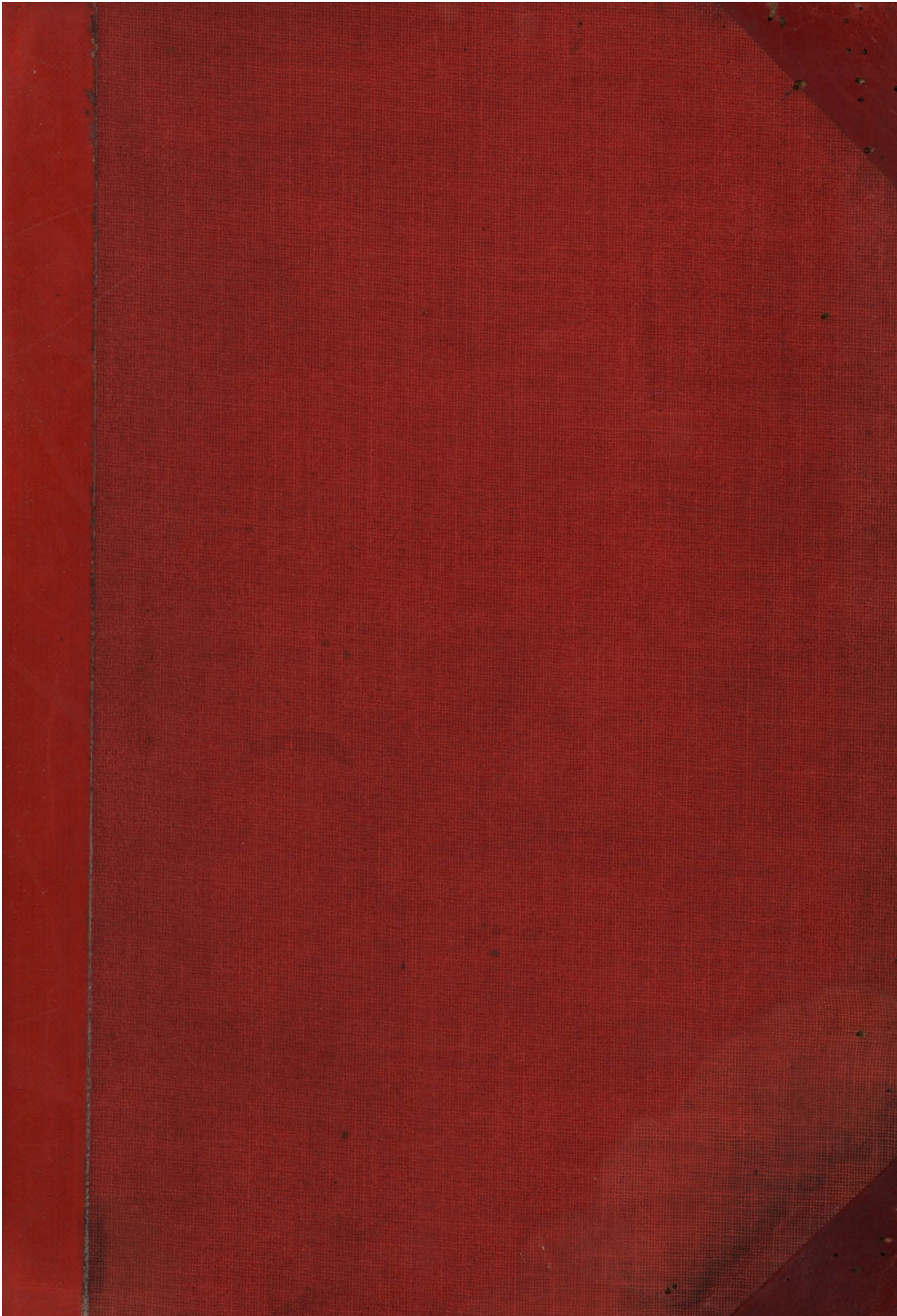

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DEPARTMENT OF SCIENCE
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THE ANALYST

THE JOURNAL OF THE

Society of Public Analysts and other Analytical Chemists

A MONTHLY JOURNAL DEVOTED TO THE ADVANCEMENT OF ANALYTICAL CHEMISTRY

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LIST OF PAPERS PUBLISHED IN *THE ANALYST* DURING 1938

The Ascorbic Acid Content of Fruits and Vegetables. By Mamie Olliver, M.Sc., A.I.C.

The Acidity of Paper. By Donald Burton, M.B.E., D.Sc., F.I.C.

The Determination of Tannins in Cacao Kernel. By D. W. Duthie, M.A., Ph.D., A.I.C.

The Determination of Sodium in Aluminium and Aluminium-Silicon Alloys. By G. B. Brook, F.I.C., G. H. Stott, M.Sc., F.I.C., and A. C. Coates, B.Sc., A.I.C.

The Contamination of Whale Oil with Fuel Oil. By E. R. Bolton, F.I.C., M.I.Chem.E., and K. A. Williams, B.Sc., F.I.C.

A Method for the Routine Determination of Glycogen in Oysters. By John P. Tully.

The Excretion of Sodium Cyanide when Administered Intravenously in Small Doses. By G. V. James, M.Sc., F.I.C.

The Electrical Deposition and Determination of Arsenic. By Sydney Torrance, A.R.C.S., B.Sc., D.I.C.

A Rapid Method for the Determination of Bismuth in Copper, Brasses, Bronzes, etc. By H. R. Fitter.

A Colorimetric Test for the Detection of Para-Hydroxybenzoic Acid in the Presence of Salicylic Acid. By S. G. Stevenson, M.Sc., B.Pharm., F.I.C., and J. C. L. Resuggan.

The Gold Number in Analytical Practice. By James Frederick Morse.

The Micro-Electrolytic Determination of Copper in the Presence of Other Metals by Controlled Potential. By A. J. Lindsey, Ph.D., M.Sc., A.I.C.

A Contribution to Water Analysis. By W. H. Kitto, M.Sc.

The Complete Analysis of Chromite. By C. F. J. Van der Walt, M.Sc.

The Determination of Bismuth in Biological Materials. By Sidney Lionel Tompsett, Ph.D., B.Sc., F.I.C.

A Test for Traces of Oxidising Agents in Milk. By R. C. Wright, B.Sc., Dip. Bact., and E. B. Anderson, M.Sc., F.I.C.

The Determination of Parachlorometaxylenol in Antiseptic Solutions. By R. P. Merritt, Ph.C., and T. F. West, M.Sc., A.I.C.

The Determination of Ethylene Glycol. By R. Cuthill, M.Sc., Ph.D., A.I.C., and C. Atkins, Ph.D., A.I.C.

Fat Absorption and Metabolism. By A. C. Frazer, M.B., B.Sc., M.R.C.S., L.R.C.P.

The Influence of Feeding-stuffs on Meat. By V. C. Fishwick, N.D.A.

The Concentration of Fruit Juices by Freezing. By P. Bilham, B.Sc., F.I.C.

The Analysis of Mixtures of Glucose and Fructose with Special Reference to Honey. By C. R. Marshall, B.Sc., Ph.D., A.I.C., and A. G. Norman, D.Sc., Ph.D., F.I.C.

Coffee Extracts. By F. W. Edwards, F.I.C., and H. R. Nanji, Ph.D., D.I.C., F.I.C.

A New Volumetric Iodide Method of Determining Starch. By W. Whale.

Micro-tests for Elements in Organic Compounds. By Cecil L. Wilson, M.Sc., Ph.D.

The Gravimetric Determination of Germanium. By Glyn Rees Davies, B.Sc., Ph.D., and Sir Gilbert Morgan, O.B.E., D.Sc., F.I.C., F.R.S.

Hair Dyes. I. The Chemistry and Analysis of Henna. By H. E. Cox, D.Sc., Ph.D., F.I.C.

The Determination of Acidity in Knitted Woollen Goods. By S. R. Trotman, M.A., F.I.C., and A. Bramley.

Analysis of Vinegar. Part I. Spirit, Malt, Distilled Malt and Artificial Vinegars and their Differentiation. By F. W. Edwards, F.I.C., and H. R. Nanji, Ph.D., D.I.C., F.I.C.

Microchemical Investigations on Siliceous Dust. By Janet W. Matthews, Ph.D., D.I.C., F.I.C.

The Detection and Estimation of Ouabain and Strophanthin. By W. D. Raymond, B.Sc., A.I.C,

The Proportion of Copper present in Tomato Purée. By T. Cockburn, F.I.C., and Magnus Herd, B.Sc., F.I.C.

A Simple Gravimetric Method of Determining Copper. By P. Hersch.

The Electrolytic Analysis of Nickel Bronzes and Light Aluminium Alloys. By Sydney Torrance, A.R.C.S., B.Sc., D.I.C.

Determination of Lead in Drinking Water. By H. Ingleson, M.A., D.Phil.

An Investigation into the Methods of Toxicological Analysis of Viscera. Part II. The Extraction of Alkaloids from Viscera. By C. G. Daubney, M.Sc., F.I.C., and L. C. Nickolls, M.Sc., F.I.C.

The Determination of Aluminium in Cast Iron. By E. Taylor-Austin, A.I.C.

Determination of Nickel and Boric Acid in Nickel-plating Solutions. By G. Stanley Smith, B.Sc., A.I.C.

Citric Acid Determination in Milk and Milk Products. By Paul S. Arup, Ph.D., F.I.C.

A New Iodine Method for the Determination of Starch.

Part III. The Determination of Farinaceous Matter in Sausages, Meat Pastes and Fish Pastes, with a Note on their Analysis. By F. W. Edwards, F.I.C., H. R. Nanji, Ph.D., D.I.C., F.I.C., and W. R. Chanmugam, F.I.C.

Part IV. The Determination of Dextrin in the Presence of Starch and Sugars. By F. W. Edwards, F.I.C., H. R. Nanji, Ph.D., D.I.C., F.I.C., and W. R. Chanmugam, F.I.C.

Part V. Starch in Leaf Material. By J. J. Chinoy, M.Sc., Ph.D., D.I.C.

The Extraction of Alkaloids and Other Organic Drugs from Viscera. By F. Bamford, B.Sc.

Studies in Internal Electrolysis. IV. The Determination of Small Quantities of Mercury in the Presence of Copper and Zinc. By James G. Fife, M.Sc., F.I.C.

The Determination of Unsaponifiable Matter in Whale Oil by the Draft Method of the Norwegian Standards Association. By E. R. Bolton, F.I.C., M.I.Chem.E., and K. A. Williams, B.Sc., F.I.C.

The Determination of Minute Quantities of Gold in Urine. By A. R. Jamieson, B.Sc., F.I.C., and R. S. Watson, A.I.C.

Residual Fat in Solvent-extracted Materials. By H. C. Lockwood, B.Sc., F.I.C.

THE CHROMIUM COMPOUND OF 8-HYDROXYQUINOLINE. By E. Taylor-Austin, A.I.C.

THE RAPID DETERMINATION OF PHOSPHORUS IN MILD STEEL. By T. P. Hoar, M.A., Ph.D., B.Sc.

THE DETERMINATION OF THE ORGANIC ACIDS IN SILAGE EXTRACTS AND BACTERIAL CULTURES. By A. M. Smith, Ph.D., D.Sc., A.I.C.

THE DETERMINATION OF ACID IN WOOL. By J. Barritt, B.Sc., A.R.C.S., A.I.C., H. H. Bowen, F. L. Goodall, M.Sc., and A. Whitehead.

ANALYSIS OF COMMERCIAL LEAD. By E. A. Coakill, A.I.C.

DETERMINATION OF MAGNESIUM IN BIOLOGICAL MATERIALS. INTERFERENCE OF MANGANESE. By J. Duckworth, D.Sc., and W. Godden, B.Sc., A.R.C.S., F.I.C.

THE DETERMINATION OF NITROGEN IN MIXED FERTILISERS CONTAINING NITRATES AND CHLORIDES. By Bernard Dyer, D.Sc., F.I.C., and J. Hubert Hamence, Ph.D., M.Sc., F.I.C.

A NEW VOLUMETRIC PROCESS FOR VANADIUM. By B. S. Evans, M.C., M.B.E., D.Sc., F.I.C.

A NEW VOLUMETRIC PROCESS FOR TELLURIUM. By B. S. Evans, M.C., M.B.E., D.Sc., F.I.C.

ERRATA:

VOL. 62, 1937:

p. 257. Table VI: The heading *should read*: Approximate weight production of milk fatty acids in cows receiving 4 ozs. daily of cod-liver oil in food. (Combined milk from 2 cows collected over 4-day periods in each case.)

In the first line of the Table, *for* "Milk-fat production per day" *read* "Milk-fat production over 4-day period."

VOL. 63, 1938:

p. 177. Line 5. *For* "hydrofluoric acid" *read* "hydrochloric acid."

p. 334. Line 5. "when excess of ferrous sulphate had *not* been added." *Delete "not."*

p. 336. First line below Fig. 1. *For* "factor A_2" *read* "discrepancy factor."

p. 584. In the formula, *for* "0·605 g. of NH_4OH" *read* "0·605 g. of NH_3."

p. 612. Line 27. *For* "693$m\mu$ band" *read* "603$m\mu$ band."

p. 728. Line 1. For "*Nitragyne Speciosa*" read "*Mitragyne Speciosa.*"

p. 825. Line 11. *For* "Ce(C) 9509" *read* "CE(C) 9505."

p. 869. First line of discussion. *For* "Present day fertilisers contained very little chloride" *read* "Present day fertilisers containing nitrate contained very little chloride."

DECENNIAL INDEX, VOLS. LI–LX:

p. 22. Column 1. Callan, T., and Henderson, J. A. R. *For* "1926" *read* "1929."

p. 80. Column 2, lines 10 to 14 from the bottom. The papers on "Standards for purity of 'ethyl' vanillin," and "The detection of metallic particles" should be under the name of "Lockwood, H. C.," and not of "Lough and Lewis."

JANUARY, 1938 Vol. 63, No. 742

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held on Wednesday, December 1st, 1937, at the Chemical Society's Rooms, Burlington House, Piccadilly, W.1, the President, Dr. G. Roche Lynch, being in the chair.

Certificates were read in favour of:—John Edward Byles, B.Sc., F.I.C., William Montague Dowson, B.Sc., A.I.C., Alfonzo Matzas Fill, Joseph Frederick Hirst, B.Sc., F.I.C., Thomas Worthington Jackson, B.Sc., A.I.C., Robert Leopold Kenny, B.Sc., A.I.C., Arthur James Lindsey, Ph.D., M.Sc., A.I.C., Francis Arthur Lyne, B.Sc., A.I.C., Cecil Denis Bradley Moon, A.I.C., James William Tullo, B.Sc., F.I.C., James Norman Vickers, B.Sc., A.I.C.

The following were elected members of the Society:—Harold Firth Bamford, B.A., Cecil Robertson Bond, M.Sc.Techn., F.I.C., Frederick Alan Dawson, B.Sc., John Hawthorne, B.A., Ph.D., F.I.C., Geoffrey Moses, A.M.C.T., F.I.C., Marcus Robinson, B.Sc., A.I.C., and John Linley Wilson, M.Sc., F.I.C.

The following papers were read and discussed:—"The Detection and Determination of *p*-Hydroxybenzoic Acid in the Presence of Salicylic Acid," by S. G. Stevenson, M.Sc., B.Pharm., F.I.C., and J. Resuggan; "The Contamination of Whale Oil with Fuel Oil," Parts I and II, by E. R. Bolton, M.I.Chem.E., F.I.C., and K. A. Williams, B.Sc., F.I.C.; "The Analysis of Glucose-Fructose Mixtures, with Special Reference to Honey," by C. R. Marshall, Ph.D., A.I.C., and A. G. Norman, M.Sc., D.Sc., Ph.D., F.I.C.

SCOTTISH SECTION

AN Ordinary Meeting of the Section was held in Glasgow on November 17th, 1937.

The following papers were read and discussed:—"A Method for the Estimation of Bismuth in Biological Materials," by S. L. Tompsett, Ph.D., B.Sc., F.I.C.; "Variations in the Composition of Black-currants," by John F. Brown, B.Sc., A.I.C.

The Ascorbic Acid Content of Fruits and Vegetables

BY MAMIE OLLIVER, M.Sc., A.I.C.

(Read at the Meeting, November 3, 1937)

THE micro method for determining ascorbic acid by titration with 2:6-dichlorophenol-indophenol, developed by Harris and Ray,[1] has found wide application in the study of plant tissues. The method is simple, and numerous investigators have shown, by comparison with animal tests, that it is reliable. It has been suggested that reducing substances other than ascorbic acid may cause interference. Recently-published work, however, indicates that the amounts of interfering substances present in plant tissue are small and are insufficient to cause any serious errors in routine determinations. It has, however, been pointed out (Van Eekelen,[2] Harris[3]) that errors may be introduced by plant oxidases partially destroying the ascorbic acid during sampling and grinding. This may be avoided by rapid extraction and titration, and oxidation is also prevented by the use of metaphosphoric acid during extraction (Fujita and Iwatake,[4] Musulin and King,[5] Harris[3]).

Another source of error that may be introduced in applying this micro method to plant tissue is the failure to obtain samples which are truly representative of the material under examination. Bracewell *et al.*[6] pointed out the variation in concentration of ascorbic acid in different parts of apples. Bacharach *et al.*[7] recorded a similar variation in oranges. Uneven distribution has also been found in spinach, sprouts, runner beans and asparagus (Olliver[8]). This uneven distribution is of particular importance when comparative tests are being made, as the quantity of tissue taken for the micro determination may represent only a very small percentage of the material being used for the experiment.

The present investigations were carried out to determine the range of variations likely to occur in the ascorbic acid content of fruits and vegetables. Values obtained for different samples taken from any one batch of fruit or vegetables were to be compared in order to illustrate the necessity for representative sampling. In addition, different batches were to be tested and the effect of variations in ripeness, time of picking, size, and other conditions of the fruit or vegetable considered. The probable causes of variation in the ascorbic acid content, and the region of maximum incidence of the vitamin were other points to be investigated.

METHOD.—When applying the micro method of estimating ascorbic acid to plant tissue it is recommended that not more than 20 g. of material should be taken for extraction. Complete extraction is difficult if the concentration of material is high and, in addition, some oxidation of ascorbic acid may occur during the extra time required for grinding a larger sample. When the ascorbic acid content of the tissue is low, it has been found preferable to adjust the strength of the indicator rather than to increase the concentration of the tissue extract.

Consistent results can be obtained when sampling is guided by a knowledge of the factors affecting the distribution of ascorbic acid in the sample, but not less than four or five determinations should be carried out on every batch of fruit and vegetable examined and an average figure calculated.

It has already been shown by many workers that storage affects the concentration of ascorbic acid in plant tissue. All material tested in this work was therefore examined within a few hours of picking.

In the following estimations a 20 per cent. solution of trichloroacetic acid, mixed with a 20 per cent. solution of metaphosphoric acid, was used for the extraction. Sufficient quantities of each solution were taken to ensure that the final extract contained 5 per cent. of trichloroacetic acid and 2 per cent. of metaphosphoric acid. The weighed sample was first ground rapidly and thoroughly into a paste with 5 to 10 g. of sand and approximately one-fifth of the total amount of acid to be used, and grinding was then completed after addition of about half of the remaining acid. The mixture was filtered rapidly through fine muslin, extraction being aided by pressing the residue with a glass rod. The friable mass was returned to the mortar, and extraction was repeated with the remainder of the acid. Finally, the residue was well washed with water, and the solution was made up to the required volume. This extract was then filtered through a No. 1 Whatman filter-paper and titrated without delay.

For coloured extracts a modification of the method of McHenry and Graham[9] was used. It is usually possible to obtain a rough indication of the ascorbic acid content of the material by direct titration, provided that a control tube is used. After this preliminary titration, 2 ml. of a freshly-prepared filtered extract were placed, together with 1 ml. of chloroform, in a long-pointed centrifuge tube. The 2:6-dichlorophenol-indophenol indicator was then rapidly introduced into the upper (*i.e.* extract) layer, which was agitated by a stream of oxygen-free carbon dioxide. The indicator* was added to within 0·02–0·05 ml. of the required volume, calculated approximately from the direct titration, and the two layers were then mixed by introducing the inlet tube of the gas into the lower layer. Addition of the indicator was continued until the chloroform layer, after being mixed with the extract layer, developed a definite pink colour. Centrifuging may be required to break the emulsion in the lower layer. It is most important that the indicator and extract should be well mixed before the chloroform and aqueous layers are mixed. If the indicator comes into direct contact with the chloroform, a pink colour, not discharged by ascorbic acid, may develop.

Variation of Ascorbic Acid Content of Fruits and Vegetables with Degree of Maturity and Date of Picking

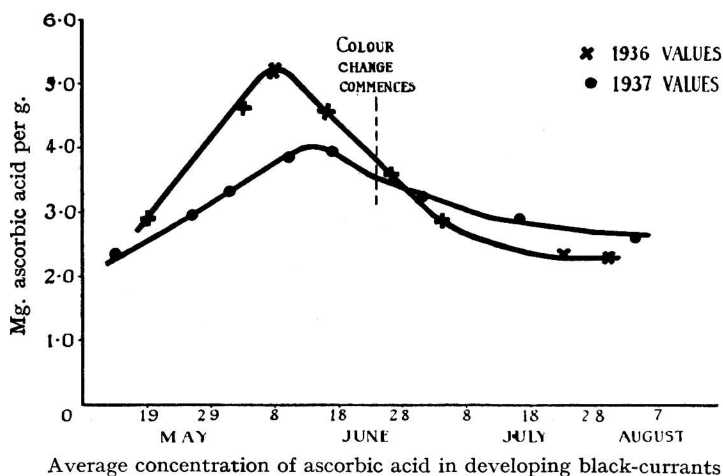
It was decided to follow the variation in the ascorbic acid content of fruits from the time of setting to final ripeness. Since, on any one day of picking, individual fruits may vary considerably from one another, both in size and degree of ripeness, tests were applied to mixed samples containing all the types picked on the day of test. Sampling was carried out at frequent intervals over

* The strength of the indicator solution (0·08 per cent.) was the same as that used by McHenry and Graham.

the whole period of development, and at least five estimations were made on each day's sample. In this way the variation in ascorbic acid content of the average fruit was followed through all stages of growth.

In addition to these estimations, a study was made of the ascorbic acid content in fruit of various sizes and degrees of ripeness on the same day of picking.

BLACK-CURRANTS.—Six-year-old bushes of Westwick Choice variety were chosen in 1936 for investigating the change in ascorbic acid content of black-currants during development. The average results obtained by representative sampling over a period of twelve weeks are plotted in Fig. 1. The experiment was repeated in 1937, but, as the old bushes were not available, smaller bushes, five years old, of the same variety and in the same field, were used. It is seen that even in early May, when the berries are only just forming, the ascorbic acid concentration is high. Subsequently the value rises, but begins to fall in the period just preceding the colour change from green to red and black. In July, when the



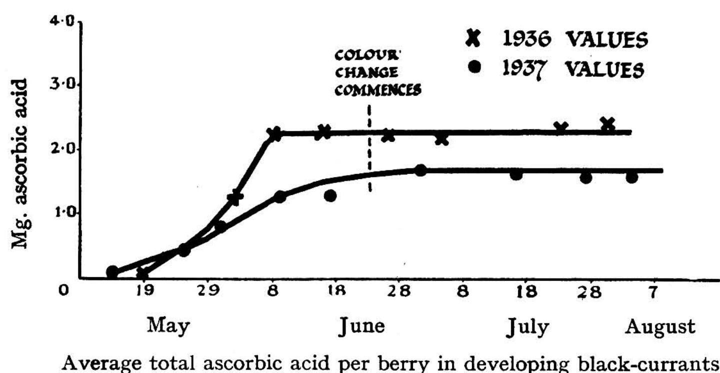
Average concentration of ascorbic acid in developing black-currants

Fig. 1.

berries are fully ripe, the average concentration is approximately equal to that of the berries in the initial stage of development. It is a point of interest that the curve for 1936 reaches a much higher peak in early June than the curve for 1937 at the same date. The initial difference between the two curves may be due either to variation in weather conditions, or to the fact that berries from smaller bushes were tested in 1937. The former would seem the more probable explanation, as a similar phenomenon has been observed in the tests on gooseberries. Wet weather, followed by a warm period, resulted in the fruit ripening earlier in 1937 than in 1936, in which year the season was wet and cold throughout.

The fall in concentration of ascorbic acid as the fruit develops may be due either to a real decrease in the total ascorbic acid present or to an apparent decrease as the result of increase in berry size. The average total amount of ascorbic acid present per berry was therefore calculated from the average weight

of the fruit tested and the average amount of ascorbic acid per gram (Fig. 2). It is seen that the average total amount of ascorbic acid per berry rapidly increases in the early stages of development, and then remains constant. Consequently, as the berries continue to increase in weight the amount of ascorbic acid per unit weight of fruit falls.



Average total ascorbic acid per berry in developing black-currants

Fig. 2.

In conjunction with the tests on these mixed samples, berries were roughly graded into various sizes to see to what extent the concentration of ascorbic acid was influenced by the size of berries in any one batch. The results given in Table I show that size of fruit is not the sole factor influencing the concentration of ascorbic acid. Not only are the results for the medium-sized berries similar to those for the small berries, but also the total ascorbic acid per berry on any one day varies considerably in fruit of different size. It is seen, however, that the concentration of ascorbic acid in the larger-sized berries is lower than in the medium and small berries.

TABLE I

EFFECT OF BERRY SIZE ON THE ASCORBIC ACID CONTENT OF BLACK-CURRANTS

Date	Condition of fruit	Ascorbic acid per g. of fruit berries			Average total ascorbic acid per berry		
		Small (0·10–0·25 g.) mg.	Medium (0·32–0·44 g.) mg.	Large (0·53–1·09 g.) mg.	Small mg.	Medium mg.	Large mg.
9.6.37	Green, unripe ..	3·82	4·02	3·66	0·38	1·28	2·04
17.6.37	Green, unripe ..	4·06	4·19	3·61	0·41	1·26	1·99
30.7.37	Black, nearly ripe	2·95	2·95	2·44	0·74	1·30	2·27
3.8.37	Black, ripe ..	2·64	2·77	2·20	0·53	1·19	2·40

This is in agreement with the results for ripe and slightly under-ripe black-currant samples of the same batch of fruit (Table II). Ripening is accompanied by a slight increase in weight, and the concentration of ascorbic acid in the slightly under-ripe fruit is found to be higher than in the ripe fruit.

TABLE II

EFFECT OF DATE OF PICKING AND DEGREE OF RIPENESS ON THE ASCORBIC ACID CONTENT OF BLACK-CURRANTS

	Date of picking 15.7.37 Ascorbic acid per g.		Date of picking 21.7.37 Ascorbic acid per g.	
	Ripe fruit mg.	Slightly under-ripe fruit mg.	Ripe fruit mg.	Slightly under-ripe fruit mg.
Baldwin variety				
Farm A	2·50	3·03	2·61	2·80
Farm B	2·37	2·59	2·25	2·38
Farm C	2·43	2·56	2·38	2·35
Farm D	2·50	2·87	2·51	2·89
Average	2·45	2·76	2·44	2·61
September black variety				
Farm E	2·46	2·63	2·35	2·67
Farm A	2·70	2·97	2·58	2·80
Farm F	2·30	2·50	2·12	2·35
Average	2·49	2·70	2·35	2·61

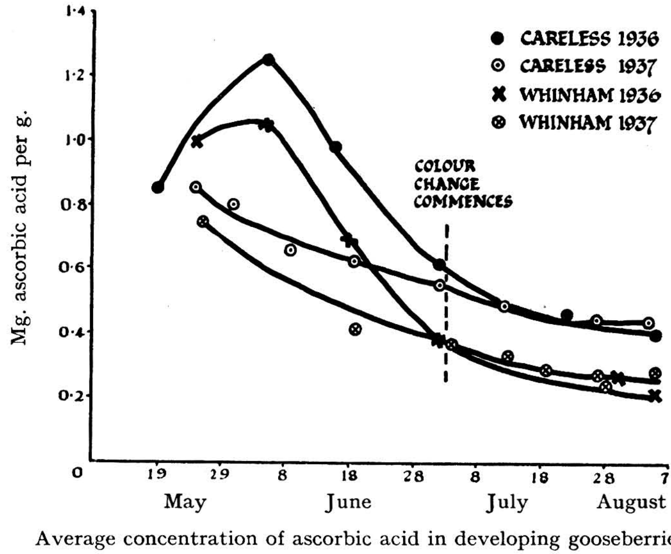
Individual berries of Westwick Choice black-currants were then tested, the whole berry being weighed and extracted in the usual way, and thence the total amount of ascorbic acid per gram estimated. The figures in Table III illustrate the great variation that may be found among individual berries picked on the same day. It is obvious that, as the concentration of ascorbic acid varies so

TABLE III

ASCORBIC ACID CONTENT OF INDIVIDUAL BLACK-CURRANT BERRIES

		Ascorbic acid per g.		
Date	Colour of berry	Small berries (0·14–0·27 g.) mg.	Medium berries (0·30–0·47 g.) mg.	Large berries (0·60–0·94 g.) mg.
7.7.37	Green ..	1·84	2·73	2·32
	Red ..	3·46	3·73	2·49
	Black ..	3·36	—	2·35
16.7.37	Green ..	2·63	3·16	—
	Purple ..	2·82	3·53	—
	Black ..	—	3·47	—
3.8.37	Red ..	2·71	2·62	—
	Purple ..	3·15	2·56	2·55
	Black ..	2·96	2·42	2·19

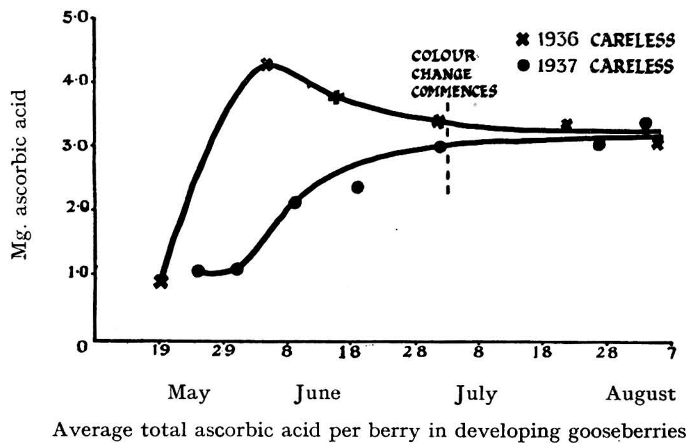
greatly between individuals, great care must be taken to obtain a sample which is truly representative of the batch of fruit under examination.



Average concentration of ascorbic acid in developing gooseberries

Fig. 3.

GOOSEBERRIES.—The concentration of ascorbic acid in developing gooseberries was determined as for black-currants. The shape of the curve plotted from the 1936 results resembles closely the black-currant curve of the same year (Fig. 3). Two varieties of fruit, Whinham and Careless, were tested simultaneously. It is seen that the values for the Whinham variety are consistently lower than those for the



Average total ascorbic acid per berry in developing gooseberries

Fig. 4.

Careless. This is an interesting point, as soil conditions for the bushes were similar, both varieties being grown in one field. The fruits themselves, however, are essentially different. Whinham gooseberries ripen at a later period than the Careless variety and, in addition, develop a red colour on ripening, whilst Careless berries become yellow. A flattening of the curve, even more marked than that observed in the **1937** black-currants, was also found for both varieties of gooseberries in **1937**. The calculated average total ascorbic acid per berry increases in the **1937** results at a rate similar to that found for black-currants of the same year (Fig. 4). The **1936** results show a rapid increase followed by a fall to a constant level.

TABLE IV

EFFECT OF BERRY SIZE ON THE ASCORBIC ACID CONTENT OF GOOSEBERRIES

Date	Condition of fruit	Ascorbic acid per g. of fruit Berries			Average total ascorbic acid per berry		
		Small mg.	Medium mg.	Large mg.	Small mg.	Medium mg.	Large mg.
Careless variety							
31.5.37	Green, hard	0·83	0·79	0·78	0·42	0·79	2·02
9.6.37	Green, hard	0·84	0·76	0·67	1·13	2·13	3·75
Whinham variety							
19.6.37	Green, hard	0·42	0·43	0·39	0·36	0·86	1·81
28.7.37	Streaked red, nearly ripe	0·29	0·21	0·22	0·80	1·19	1·78

TABLE V

ASCORBIC ACID CONTENT OF INDIVIDUAL WHINHAM GOOSEBERRIES

Date	Condition of berry	Ascorbic acid per g. Berries							
		Small mg.	Avge.	Medium mg.	Avge.	Large mg.	Avge.	Very large mg.	Avge.
2.7.37	Green, hard	0·48	0·35	0·36	0·48	0·35	0·32	—	
	Green, slightly soft	0·29		0·51		0·29		—	
	Streaked red, soft	0·27		0·58		—		0·35	
12.7.37	Green, hard	—		0·35	0·38	0·21	0·31	0·23	0·30
	Streaked red, soft	—		0·41		0·37		0·37	
	Red, ripe	—		0·39		0·36		0·30	
19.7.37	Green, hard	0·43	0·41	0·22	0·26	0·22	0·27	—	
	Streaked red, soft	0·40		0·29		0·27		—	
	Red, very ripe	0·39		0·27		0·31		—	
28.7.37	Streaked red, slightly soft	—		0·17	0·21	0·23	0·23	—	
	Red, ripe	—		0·15		0·21		—	
	Red, very ripe	—		0·31		0·26		—	

In gooseberries, as in black-currants, there is great variation in the total ascorbic acid content of berries of different weights (Table IV). From the figures given for Whinham gooseberries in this table it is seen that the amount of ascorbic acid per gram of developing fruit is again mainly influenced by the date of picking.

Individual berries were also tested, and considerable variation was found in the concentration of ascorbic acid in the different individuals. From Table V it is seen that, as the season advances, there is a marked fall in the concentration of ascorbic acid for the average of all berries of approximately the same size and also for individuals of the same degree of ripeness. On the same day of picking, however, with medium or large berries the riper fruit has, on the whole, a higher value than the unripe fruit. Similar results were obtained from tests carried out on samples of gooseberries of mixed sizes (Table VI).

TABLE VI

THE ASCORBIC ACID CONTENT OF GOOSEBERRIES OF DIFFERENT DEGREES OF RIPENESS

Ascorbic acid per g.

Whinham variety			Careless variety		
Condition of fruit	Sample A mg.	Sample B mg.	Condition of fruit	Sample A mg.	Sample B mg.
Green, hard	0·22	0·27	Green, slightly soft	0·40	0·35
Streaked red, soft	0·24	0·28	Yellowish-green, soft	0·45	0·41
Red, ripe	0·33	0·30	Yellow, ripe	0·50	0·55

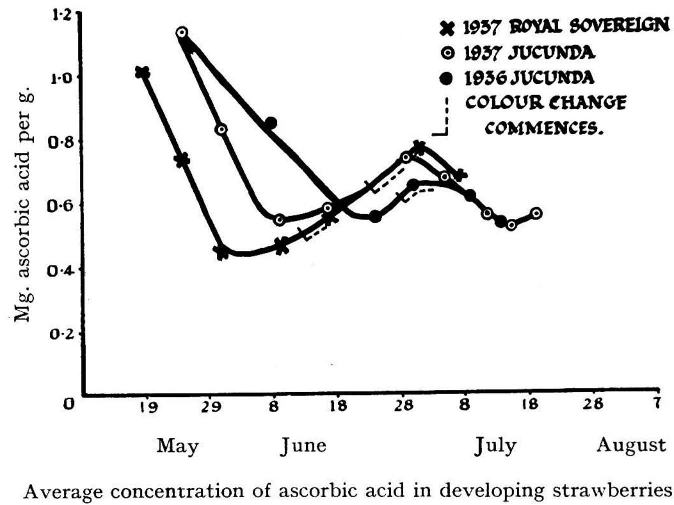
Two main opposing factors, therefore, appear to influence the concentration of ascorbic acid in gooseberries. One results in a decrease in average concentration as the season progresses, and the other causes an increase in concentration in the riper, as compared with the less ripe, fruit on the same day. This increase on ripening is probably related to surface concentration of ascorbic acid. Rudra[10] has found that in many Indian fruits the ascorbic acid is more concentrated in the skin than in the edible portion. The present tests show that in gooseberries the vitamin is more concentrated in the outer tissues of the berry, and, in addition, the concentration in the outer tissue is much higher in the riper than in the less ripe fruit (Table VII).

TABLE VII

THE DISTRIBUTION OF ASCORBIC ACID IN INDIVIDUAL WHINHAM GOOSEBERRIES

Condition of berry	Ascorbic acid per g. — Inner tissue of berry (pulp and seeds) mg.	Outer tissue of berry mg.	Calculated on whole berry mg.
Green, turning red	0·19	0·24	0·22
Pale red, slightly under-ripe	0·15	0·26	0·22
Dark red, ripe	0·14	0·34	0·24
Dark red, very ripe	0·19	0·43	0·31

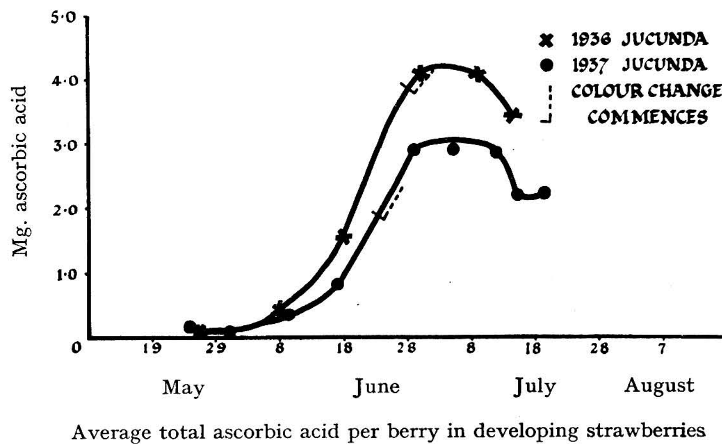
To summarise these results, it would seem that, with gooseberries, the later the picking, the lower is the average concentration of ascorbic acid in the fruit, although for the same day's picking, the riper fruit is richer in ascorbic acid than the less ripe.



Average concentration of ascorbic acid in developing strawberries

Fig. 5.

STRAWBERRIES.—The variation in the ascorbic acid content of strawberries during development and ripening of the fruit was followed by frequent testing, as



Average total ascorbic acid per berry in developing strawberries

Fig. 6.

previously described. The resulting curves differ appreciably from those for black-currants and gooseberries (Fig. 5). The concentration of ascorbic acid in the berries is initially very high, but falls rapidly in the first stage of berry development, rising again as the fruit begins to ripen and subsequently falling as the season progresses. The strawberries tested in 1936 were Jucundas. In 1937, berries from the same plants were again tested and gave a similar curve for the concentration of ascorbic acid in the fruit, except that the whole curve was displaced to the left. It is probable that this effect is due to the earlier ripening of the berries in 1937, as compared with 1936. Royal Sovereign strawberries, a much earlier variety than Jucunda, taken in 1937 from plants grown in the same field, gave results similar to the Jucundas, but, again, the curve was displaced to the left.

The average total amount of ascorbic acid per berry remains very low until the fruit begins to change colour, when there is rapid increase in the value (Fig. 6). Towards the end of the season the average total ascorbic acid content per berry falls.

Tests carried out on individual strawberries confirmed the result that the early stages of ripening are accompanied by an appreciable increase in the amount of ascorbic acid per gram of fruit (Table VIII).

TABLE VIII

THE ASORBIC ACID CONTENT OF INDIVIDUAL JUCUNDA STRAWBERRIES AT DIFFERENT STAGES OF RIPENESS

	Ascorbic acid per g. of fruit						
	Green mg.	White mg.	Half red, half white mg.	Nearly red mg.	Orange-red mg.	Red, ripe mg.	Red, very ripe mg.
(*a*)	0·62	0·73	0·87	0·87	0·80	0·89	0·80
(*b*)	0·63	0·72	0·70	0·85	0·90	0·74	0·86
(*c*)	0·61	0·80	—	0·66	0·67	—	0·87
	Calculated total ascorbic acid per berry						
	mg.	mg.	mg.	mg.	mg.	mg.	mg.
(*a*)	1·45	3·75	4·36	7·79	9·05	10·50	8·60
(*b*)	1·16	5·57	2·81	6·47	10·99	7·01	5·59
(*c*)	1·56	4·11	—	7·40	7·51	—	4·89

As strawberries ripen unevenly, these results suggested that uneven distribution of ascorbic acid might be found in individual berries. Individual strawberries were therefore cut in half, and estimations were made on each half. In order to avoid oxidation as far as possible, the cut halves were immersed, immediately after weighing, in trichloroacetic acid and metaphosphoric acid solution. The results, which are given in Table IX, show that the riper side contains a higher concentration of ascorbic acid than the less ripe side. The values for the halves are found to approximate more nearly to one another with fruit in which it was impossible to detect any difference in the degree of ripeness of each half, *e.g.* with green or white fruit.

TABLE IX

DISTRIBUTION OF ASCORBIC ACID IN INDIVIDUAL JUCUNDA STRAWBERRIES. DETERMINATIONS ON SEPARATE HALVES OF BERRIES

	Ascorbic acid per g.									
	Green berries		White berries		White and red berries		Red berries		Red, ripe berries	
	Half *a*	Half *b*	Half *a*	Half *b*	White half	Red half	Half *a*	Half *b*	Less ripe half	Riper half
Berry (1), mg.	0·59	0·66	0·77	0·70	0·79	0·95	0·80	0·80	0·81	0·92
Berry (2), mg.	0·60	0·66	0·58	0·71	0·62	0·88	0·89	0·92	0·78	0·83
Berry (3), mg.	0·62	0·59	0·74	0·85	0·79	0·93	0·89	0·89	0·82	0·93

These results naturally led to investigation of the outside of berries, as compared with the inside (Table X). The high concentration of ascorbic acid in the outer tissue is very striking in the red berries, but it is seen that, even in the green fruit, the outer tissue is slightly richer in ascorbic acid than the inner portion.

TABLE X

DISTRIBUTION OF ASCORBIC ACID IN INDIVIDUAL JUCUNDA STRAWBERRIES. DETERMINATIONS ON INNER AND OUTER TISSUE OF BERRIES

	Ascorbic acid per g.								
	Green berries			White berries			Red berries		
	Outer	Inner	Calculated on whole berry	Outer	Inner	Calculated on whole berry	Outer	Inner	Calculated on whole berry
Berry (1), mg.	0·56	0·41	0·47	0·94	0·55	0·69	1·13	0·66	0·81
Berry (2), mg.	0·65	0·38	0·49	0·96	0·47	0·71	1·05	0·57	0·75
Berry (3), mg.	—	—	—	0·69	0·39	0·50	1·32	0·66	0·95

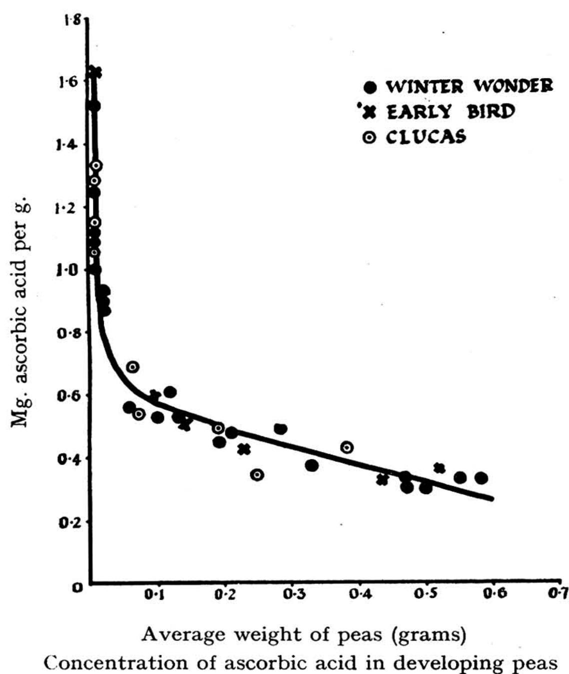
On summarising these results it would appear that the ascorbic acid concentration of strawberries of early crops is higher than that of later crops, although for any one day's picking the riper berries usually have a higher concentration of ascorbic acid than the less ripe. The figures that have been obtained are especially important in demonstrating the great care needed in sampling when testing strawberries for ascorbic acid content by the micro method. It is essential that the material taken should be representative, not only of berries of different sizes and degrees of ripeness, but also of the inside and outside of the berry.

PEAS.—It was decided to confine the investigation on peas to a study of the effect of size on the ascorbic acid content of the tissue at different dates of picking. Samples were taken from three varieties of peas, grown side by side in one large field.

Tests were carried out over a period of five to six weeks, beginning while the flowers were still on the vines. On each day of picking, the peas were graded into various sizes, and the average concentration of ascorbic acid in the different-sized peas was estimated. The results show that the weight of the pea, irrespective of

the date of sampling, is the main factor determining the concentration of ascorbic acid (Fig. 7).

The high values obtained for the small seeds are especially striking. As the weight of the pea increases, the concentration of ascorbic acid falls, very rapidly during the initial stages of development and then more gradually after the average weight of the pea has reached approximately 1 gram. These results are especially interesting in view of the findings of Mack and Tressler[11] in America on peas at the harvesting stage. These workers found that early, small-seeded varieties of peas were better sources of the vitamin than the late, large-seeded varieties. Also, in any variety, the percentage of ascorbic acid was inversely proportional to the sieve-size of the peas.



Average weight of peas (grams)
Concentration of ascorbic acid in developing peas

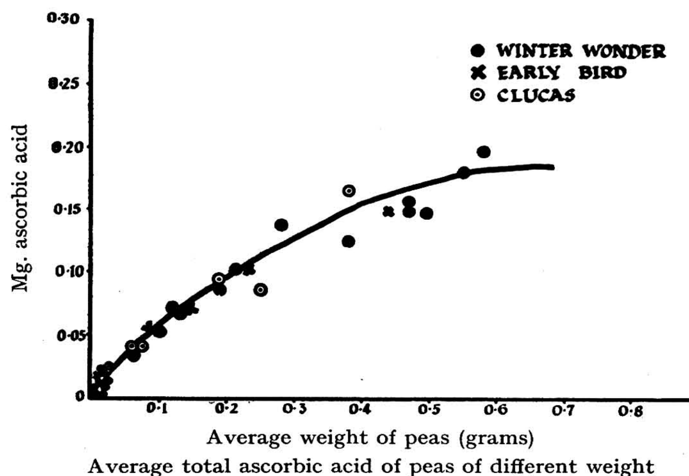
Fig. 7.

The results in the present work have shown that the amount of ascorbic acid per gram of tissue falls as the weight of the pea increases. It is also seen from these results that this fall in concentration is accompanied by an increase in the total amount of ascorbic acid per pea (Fig. 8).

POTATOES.—It has been suggested in many theses that the formation of ascorbic acid accompanies metabolic activity. The results obtained in this present work tend to confirm this suggestion. In the seeds and fruits studied already, considerable metabolic activity would be expected throughout development, and it was therefore considered interesting to investigate the change in the ascorbic acid content of a storage organ.

Potatoes were chosen for the purpose, and samples were taken from a field

of King Edward plants. The ascorbic acid concentration was determined at intervals over a period of four months, samples in every instance being tested within a few hours of lifting. The constant results obtained at all dates of sampling during the period and for all sizes of potatoes are striking (Table XI). Thus the average values for the tiny, developing tubers agree closely with those obtained



Average total ascorbic acid of peas of different weight

Fig. 8.

for large fully-developed potatoes. These results are of great interest when compared with the variations found in the ascorbic acid content of the seeds and fruits.

TABLE XI

ASCORBIC ACID CONTENT OF KING EDWARD POTATOES AT VARIOUS STAGES OF DEVELOPMENT

Date	No. of samples tested	Range in ascorbic acid per g. mg.	Average ascorbic acid per g. mg.	Range in weights of potatoes tested g.
4.6.36	3	0·26–0·33	0·30	< 1–1
22.6.36	3	0·32–0·34	0·33	2–21
13.7.36	4	0·25–0·33	0·29	< 1–51
6.8.36	4	0·32–0·40	0·30	24–124
27.8.36	8	0·28–0·34	0·31	51–256
30.9.36	8	0·23–0·31	0·29	11–158

ASPARAGUS.—The high concentration of ascorbic acid found in green tissue has suggested the association of chlorophyll with the production of the vitamin. It would seem more probable, however, from the results obtained in this investigation that ascorbic acid is connected rather with metabolic activity than with pigment formation. This view is supported by tests carried out on asparagus. It has already been shown (Olliver[9]) that the concentration of ascorbic acid decreases progressively from the tip down the stem. Further tests have shown

that the tips of asparagus shoots are consistently rich in ascorbic acid, even before chlorophyll or any other pigment is produced (Table XII).

TABLE XII

DISTRIBUTION OF ASCORBIC ACID IN DEVELOPING ASPARAGUS SHOOTS

Condition of shoot	Ascorbic acid per g. Tips mg.	Green stem mg.	White stem mg.
Very young. No colour	1·00	—	—
Very young. Shoot tipped faint mauve ..	0·85	—	0·27
Young. Deep purple tip. No green ..	1·11	—	0·29
Young. Shoot showing green	1·30	0·62	0·20
Full-grown for cutting. Slender shoot ..	1·21	0·73	0·17
Full-grown for cutting. Thick shoot ..	0·87	0·47	0·15

VARIETY OF FRUIT.—It has been shown that a marked difference exists between the concentration of ascorbic acid in Whinham and Careless gooseberries at the same degree of ripeness. The effect of variety has also been studied with black-currants and strawberries. It was realised that it would be preferable, in view of the variation in results according to the time of picking, to follow, for each variety under test, the entire growth-curve throughout the season. As it was not possible to do this, it was decided that information of a practical nature would be best obtained by testing different varieties from many sources, keeping as far as possible to a definite standard of ripeness.

In the tests on strawberries the berries sampled were all fully ripe, but showed no signs of over-ripeness. On the average values obtained, Royal Sovereign had the highest concentration of ascorbic acid (Table XIII). The variation, however, between the ascorbic acid concentrations of different samples of the same variety is very marked. The range of values for any one variety is much greater than the range of the average values for all varieties. It is therefore concluded that, with strawberries, the effect of variety on the ascorbic acid content of the fruit is much less than that of other factors which may be concerned.

TABLE XIII

ASCORBIC ACID CONTENT OF RIPE STRAWBERRIES OF DIFFERENT VARIETIES

Variety	Number of different farms supplying samples	Number of different batches tested	Ascorbic acid per g. Range of values mg.	Average value mg.
Royal Sovereign	8	17	0·44–0·88	0·69
Jucunda ..	6	19	0·50–0·83	0·62
Paxton	2	5	0·53–0·93	0·61
Evern	3	7	0·51–0·58	0·55
Brenda Gautrey	2	6	0·52–0·61	0·56

From tests made on black-currants a similar conclusion may be drawn (Table XIV). The Edina variety, however, is definitely lower in ascorbic acid content than the other varieties tested, both in individual and in average values. The low ascorbic acid content in the juice from Edina black-currants, compared with that from other black-currants, has also been observed by Charley.[12]

TABLE XIV

ASCORBIC ACID CONTENT OF RIPE BLACK-CURRANTS OF DIFFERENT VARIETIES

Variety	Number of different farms supplying samples	Number of different batches tested	Ascorbic acid per g. Range of values mg.	Ascorbic acid per g. Average value mg.
Baldwin ..	5	9	2·28–3·27	2·61
September Black	6	11	2·12–3·44	2·59
Westwick Choice	2	7	2·12–3·00	2·57
Unnamed variety	2	4	2·06–2·58	2·30
Wellington ..	2	3	2·14–2·38	2·28
Edina	3	3	1·08–1·96	1·51

It is possible that soil is an influencing factor. Three varieties of black-currants from one field all gave results similar to one another, although differing from the same varieties in other fields. Further work is needed to confirm this suggestion.

DISCUSSION AND SUMMARY.—The results obtained from this investigation illustrate the need for caution when drawing conclusions from the determination of the ascorbic acid content of plant tissue. This applies especially when the effect of different conditions of cultivation or treatment of fruits or vegetables is being studied. In such circumstances it is essential that the variation due to factors other than those under investigation should be considered. Stress is also laid on the need for representative sampling, in view of the wide variation in the concentration of ascorbic acid in different individuals. Results obtained from different parts of the same individual may also vary considerably. The concentration of ascorbic acid, for instance, is found to be higher in the outer than in the inner tissue of both strawberries and gooseberries.

From the biochemical aspect the results are interesting in demonstrating the possible connection between ascorbic acid formation and metabolic activity. The average concentration of ascorbic acid in gooseberries and black-currants rises in the initial stages of development and then falls as the season progresses. The results for strawberries are somewhat different, as it is found that the concentration of ascorbic acid falls during the early stages of development and then rises as colour-change takes place. Subsequently, the average value falls, so that berries of the later crop are not so rich in ascorbic acid as those of the early crop. In both gooseberries and black-currants the average total amount of ascorbic acid per berry increases with development of the fruit, until a steady level is reached. Strawberries show a similar increase in value, but this decreases towards the end of the season. The results obtained for ripening fruit suggest that the association

between ascorbic acid production and pigment development is incidental to the change in metabolic activity. This view is supported by the high results obtained for asparagus tips before pigment-production and by the results of tests on potatoes.

A high concentration of ascorbic acid has been found in very small peas, but the concentration falls with increase in the weight of the seed. Potatoes, taken as examples of a storage organ, have been found to contain an approximately constant concentration of ascorbic acid, independent of the size and stage of development of the tuber.

Several points of interest from the nutritional aspect are suggested. With black-currants, gooseberries and strawberries the maximum vitamin C content is obtained by early picking. This is especially interesting, in view of the fact that early picking is favoured when the fruit is to be used for bottling and canning. On any one day of picking, however, the concentration of ascorbic acid in the riper fruit of both strawberries and gooseberries is greater than that in the less ripe. Small young peas are richer in the vitamin than large, older peas. Variety, as observed with Careless and Whinham gooseberries, may be an important factor in affecting the ascorbic acid content of the fruit. With strawberries and the majority of black-currants tested, however, variety appears to have less effect on the concentration of ascorbic acid in the tissue than other factors which may be involved.

In conclusion, I wish to express my thanks to Messrs. Chivers & Sons, Ltd. for permission to carry out this work and to present these results, and to Dr. L. J. Harris for his continued interest in this work.

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Discussion

Mr. F. HIRST said that he had been very interested in Miss Olliver's paper, which was essentially a continuation of her previous work on the effect of cooking and canning on the ascorbic acid content of fruits and vegetables. He was very surprised to learn of the differences in the ascorbic acid content of the gooseberry varieties "Whinhams" and "Careless"; it was rather difficult to understand the great variations in the results obtained with berries of the same variety of fruit

at different times. Miss Olliver had laid stress on the importance of representative sampling, but he wondered if there were some other factor which had as yet not been discovered, as it did not appear feasible that sampling could be entirely responsible. The comparison of the ascorbic acid content of the different varieties of fruits was most interesting, as much work had been carried out at the Campden Research Station in testing the suitability of different varieties for canning, but they had not yet got so far as comparing the nutritional value of the many different varieties. This opened up a very wide field, and he felt that they had only just entered the gate.

Mr. G. N. GRINLING asked if Miss Olliver had followed up her work by direct canning tests afterwards. Had subsequent tests been applied to any varieties to see whether any changes had taken place?

Mr. H. T. CRANFIELD asked if any of the results had been calculated on the dry-matter basis. Owing to the variation in water-content, this was useful for the comparison of results.

Mr. A. L. BACHARACH considered that Messrs. Chivers were to be congratulated on having allowed Miss Olliver to use the valuable opportunity presented by the accessibility of fresh fruit in large quantities. The kind of information thus obtained was only possible from collaboration between those who possessed the necessary technique and scientific knowledge and those who could make available the necessary experimental material. Miss Olliver was also to be congratulated especially on her unselfishness in looking at this problem from the point of view of the plant; the role played by ascorbic acid in the developing plant could only be elucidated on the basis of work, always laborious and sometimes tedious, of the kind so excellently carried out by the author.

Mr. N. EVERS asked if any work had been done at different times during the 24 hours. If the amount of ascorbic acid depended on the balance between the amount in the fruit and the amount being used up, this would seem to be interesting.

Miss OLLIVER, replying, said that she had not systematically studied the comparative loss of ascorbic acid on canning different varieties of fruit or vegetables. The experiments which she had carried out, however, suggested that this loss was less affected by variety than by other factors, such as heat treatment before packing and head space in the can. The suggestion of calculating results on a dry-matter basis was an interesting point which she had not considered in her work. In reply to Mr. Hirst, she explained that she had not put forward sampling to account for the variation observed in the results given in the present paper. The reasons for this variation still remained to be investigated. The fact that such variation existed, however, made it important that sampling should be representative when this micro-method was used.

The Acidity of Paper

BY DONALD BURTON, M.B.E., D.Sc., F.I.C.

(Read at the Meeting of the North of England Section, April **10, 1937)**

THE problem of the measurement of the acidity of paper has, of course, received much attention from those associated with paper manufacture. The Public Analyst is concerned with the suitability of paper mainly from the consumer's point of view. Acidity is harmful in wrapping papers (especially for food and metal goods) and papers for use with printers' type and plates. The question of discoloration and deterioration during ageing or storage is important with some varieties of paper, and this is related to their acidity and the rate at which they take up acid from the atmosphere. It is obvious that the problem is complicated and that a clear conception of what is meant by the acidity of paper and "acid-free" paper is necessary. In making some papers from wood, acid is introduced as the result of treatment with bisulphites and sulphur dioxide to remove the lignin from the cellulose pulp. According to Phillips,[1] Freudenberg considered that lignin probably consisted of units

$$-O-C_6H_3(OCH_3)-CH_2-CHOH-CH_2-O-$$

joined together in chains containing ten units, and gave a soluble lignin sulphonic acid,

$$-O-C_6H_3(OCH_3)-CH_2-CH(SO_3H)-CH_2-O-$$

Recent work* has shown that this is more complex. "Encrusting substances" built up from hexoses, pentoses and uronic acids, such as glycuronic acid (I),

```
        CH.OH
       /     \
  CH.OH       O
    |         |
  CH.OH     CH.COOH
       \     /
        CH.OH
```

(I)

are also present in wood. In bleaching by chlorine or bleaching powder, acids may be produced by oxidation, and sulphuric acid may be added to speed up the process with bleaching powder. Sizing is necessary to render the final paper sufficiently water-resistant to take writing ink. Rosin boiled with sodium carbonate or water-glass may be used. Aluminium sulphate is added before or after sizing. Aluminium oxide, rosin or aluminium resinate, or silica, may be present in the paper. Loading agents, including calcium carbonate, are frequently added. Thus, paper may contain a variety of acids if they are not removed in manufacture.

* *Collegium*, 1937, 3.

The problem is similar in some respects to the one which has confronted leather chemists in relation to book-binding and upholstery leathers. The reddening and rotting of the bindings of old books is well known, and hide suites of furniture sometimes deteriorate. After investigations extending over one hundred years, it is now generally considered that this deterioration is connected with the acidity of the leather. Some modern leathers are protected from gas fumes and acid in the atmosphere by treatment with salts of organic acids, such as sodium lactate, citrate or formate. Several methods have been evolved for determining the acidity of leather, and it is thought that they may be applicable to paper.

The subject may best be considered from the following points of view: (i) The determination of the total amount of acid in paper; (ii) the determination of the *p*H of the aqueous extract; (iii) the determination of the actual *p*H of the paper.

I. The Determination of the Total Amount of Acid in Paper.—In 1931 the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry studied four methods, including the one suggested by the American Society for Testing Materials (A.S.T.M.). In 1932 they put forward the following tentative official standard method.[2]

The sample is first completely disintegrated in a special grinder of the Koerner type,[3] and the total acidity is determined by the method described by Kohler and Hall,[4] with some modifications developed at the U.S.A. Bureau of Standards. A weighed quantity of the sample is placed in a 500-ml. Erlenmeyer flask, and 250 ml. of boiling distilled water are added. The tendency of the fibres to float on the surface can be avoided by first adding small portions of the water and shaking well until the pulp is thoroughly saturated, and then adding the remainder of the 250 ml. A stopper holding a narrow glass tube, about three-quarters of a metre in length, is then affixed to the flask to serve as a condenser. The flask is heated in a bath at 95–100° C. for one hour, with occasional shaking. Its contents are poured on to a Buchner funnel (without a filter-paper), and the fibres remaining in the flask are washed into the funnel with 10 ml. of water. Strong suction is applied to the fibres, which are then returned to the flask. The extract is cooled rapidly and titrated with $N/100$ sodium hydroxide solution as soon as it reaches room temperature, phenolphthalein being used as indicator. Two additional extractions and titrations are made. A blank titration on 250 ml. of the water, which has been heated for one hour in the same glassware at 95–100° C., is made. Each test result reported must be the average of at least two determinations, and these must agree to within 0·01. This "TAPPI Method" gives the total acidity, but does not indicate whether the acid is weak or strong. Acids as weak as boric acid may be harmless, whilst sulphuric acid would certainly be undesirable.

II. The Determination of the *p*H Value of the Water Extract.—Berndt[5] has described the different methods of *p*H measurement and laid stress upon the need for standardised conditions. Titration after a one-hour hot extraction has been found to give higher results than a 24-hour cold extraction. Wulff's membrane colorimeter, having a *p*H range of 1·4 to 12·6, is held to be useful when applied to turbid liquids. Tödt's surface indicator method has been found to give lower results than extraction methods, which suggests that in that method

not all the acid is extracted. Browning and Ulm[6] have made a critical survey of existing work, and have studied the variables affecting the TAPPI standard method as applied to three papers having *p*H values of 4·7, 5·2 and 6·0. They recommend that the paper should be cut, not shredded, that the temperature of the extraction should be controlled to within ±1° C., and that the measurements should be made as rapidly as possible after extraction. The first extract contains, in the main, weak acids, and the stronger acids are then removed in subsequent extracts. Munds[7] has made the interesting observation that a lower *p*H, as measured by the quinhydrone electrode, is obtained by potassium chloride extraction than by water extraction. Leitz and Kove[8] and Chalon[9] have also dealt with *p*H control.

The British Standard Specification for Papers (Unvarnished) for Electrical Purposes, issued by the British Standards Institution in September, 1936, gives the following method:—Two g. of paper are cut into strips, about 20 mm. by 3 mm., and put into a 250–ml. round-bottomed high-grade resistance glass or quartz flask, fitted with a "ground-in" reflux condenser of the same quality of glass or quartz, which has previously been subjected to a blank test and found to give a neutral value. One hundred ml. of neutral water, free from carbon dioxide, are added, and the water is heated to boiling over a flame arranged not to char the paper. Boiling is continued for 5 minutes. The water is then cooled and decanted from the paper. The *p*H should preferably be determined by an electrometric method, but a specified colorimetric method may be used.

It seems possible that some information regarding the strength of the acid present in the aqueous extract may be obtained by applying the method which Innes devised for leather.[10] This is based on the fact that a strong mineral acid, such as sulphuric acid, increases in *p*H by practically one unit on being diluted ten times, whilst a weak acid, such as acetic, after similar dilution increases in *p*H by only 0·5 units. If the difference between the initial *p*H and the *p*H after tenfold dilution is less than 0·6, the leather is to be regarded as free from mineral or other harmful acid. If the difference figure is 0·7 or greater, the criterion of harmful acidity is the initial *p*H. In that event, leathers with an initial *p*H of 3·0 or over are regarded as free from mineral acid, whilst an initial *p*H below 3·0 indicates the presence of harmful quantities of mineral acid.

III. The Determination of the Actual *p*H of the Paper.—(*a*) *Edge's Method.*—Edge concluded that even boiling water does not extract anything approaching the whole of the acid from paper.[11] He pointed out that the acidity does not consist entirely of aluminium sulphate and sulphuric acid, and therefore made a complete electrometric titration of a known weight of the paper in a given volume of water, keeping the paper present all the time. The *p*H of the extracting water was varied by adding varying amounts of $N/100$ acid or alkali. The mixtures were allowed to stand for 24 hours in the cold, with occasional stirring, and the *p*H values were determined by means of the antimony electrode. It was thus possible to determine the *p*H of a solution in which no change took place on immersing the paper, *i.e.* the *p*H of the paper. Unfortunately, the antimony electrode reading varied with the time elapsing between immersion in the liquid and recording the millivolts.

(*b*) *Indicator Method.*—The "spotting" method has been standardised in the B.S.I. Specification. It is not regarded as giving a figure for the *p*H of paper, but is stated to indicate an upper or lower limit to which the paper should conform. If the indicators are not prepared as specified, the *p*H of the indicator (not an approximate indication of the *p*H of the paper) is obtained. Distilled water having a *p*H not less than 6·6 must be used. The indicators themselves must be half neutralised with strong alkali. Only a minute quantity is used in a test, but even this has a distinct buffer action with solutions containing very small quantities of acid or alkali. Thus, it is advisable to confirm the apparent *p*H obtained with one indicator by the use of another indicator with a different *p*H range. A large drop of the freshly prepared indicator solution is placed on the paper and spread gently, so that some is absorbed by the surface of the paper. The alteration in colour of the indicator, if any, must be observed at once and compared with the change in a drop placed on a glazed white tile, in order to eliminate the effects due to the absorption of carbon dioxide from the air. For a "neutral" paper (*p*H 5·6 being adopted for neutrality for this test), the spot, in daylight, or with a standard daylight lamp, will show the approximate colour given in the second column of the following table:

Indicator	Colour for "neutral" paper (*p*H 5·6)	*p*H range
Bromophenol blue ..	Remains blue, does not turn yellow..	3·0 to 4·6
Bromocresol green ..	Blue tinge remains, no yellow ..	3·6 to 5·2
Bromocresol purple ..	Dirty yellow, no purple tinge ..	5·2 to 6·8
Phenol red ..	Yellow, not red	6·8 to 8·4

(*c*) *Suggested Methods for Determining the Actual pH Value* (*or, more accurately, the Acid Figure*) *of Paper.*—(1) *Sorting test for a series of samples.*—The problem in determining the *p*H of paper is to equalise the *p*H inside the paper and that of a medium in which it is placed, without altering the actual *p*H of the paper. It is a well-known fact that there is a considerable difference in *p*H inside and outside gelatin when it is immersed in a dilute solution of hydrochloric acid. Loeb showed that this difference became negligible when $M/10$ sodium chloride solution was added. Atkin and Campos[12] made use of this fact in the titration of hide powder; its *p*H may be determined as follows:—The powder (7 g.) is allowed to stand in contact with 100 ml. of $M/10$ potassium chloride solution for 24 hours, with occasional shaking, the potassium chloride having previously been brought to *p*H 5·5 by means of $N/100$ acetic acid. The mixture is filtered through a paper previously washed with the above-mentioned potassium chloride solution of *p*H 5·5, and the *p*H of the filtrate is determined, preferably with the glass electrode. This method seems to furnish a simple test for use in sorting papers when a series has to be examined. In some preliminary experiments, 3 g. of the paper were allowed to stand in contact with 100 ml. of $M/10$ potassium chloride solution for 48 hours, with occasional shaking. The liquid was then decanted, and its *p*H was determined with the glass electrode. The question whether potassium chloride is the best solution to use was considered. It has a *p*H of 5·4, and it seemed that an unbuffered salt solution of slightly higher *p*H might be better, since paper has

a small reserve of acidity. Further determinations with $M/10$ magnesium sulphate and $M/10$ sodium chloride solutions were therefore made, with the following results:

TABLE I

	$M/10$ potassium chloride	$M/10$ magnesium sulphate	$M/10$ sodium chloride
*p*H of solution	5·4	5·4	5·2
*p*H of solution after paper had been immersed in it for 48 hours at 20° C. ..	3·6	3·9	3·7
*p*H after cooling the solution in which the paper (3 g. per 100 ml.) had been boiled for 1 hour	3·7	3·7	3·6

All the solutions therefore give practically the same result, and the sample of blotting paper used was decidedly acid.

(2) *Method for determining the actual pH, or acid figure, of paper.*—In 1929 an accurate method of determining the acid figure, or *p*H, of vegetable-tanned leather was devised by Atkin and Thompson[13]; this made use of the equalising effect of $M/10$ potassium chloride solution, and the fact that a straight line is obtained when a series of dilutions of a liquor is made and the *p*H values are plotted against the logarithms of these dilutions. Quantities of 1, 2 and 4 g. of finely divided leather are separately placed in resistance-glass flasks fitted with paraffined corks. To each lot of leather 100 ml. of $M/10$ potassium chloride solution (analytical reagent quality) are added. After standing at laboratory temperature for 24 hours, with occasional shaking, the solution is carefully decanted from the leather, and the *p*H is determined with the glass electrode. The *p*H values so obtained are then plotted against the logarithms of the dilutions of the water in the original leather. For example, when 2 g. of leather containing 14 per cent. of moisture (*i.e.* 0·28 g. or 0·28 ml. of water) are extracted with 100 ml. of $M/10$ potassium chloride solution, the amount of liquid in contact with the leather is 100·28 ml. This represents an increase in the original moisture in 2 g. of leather of 100·28/0·28, or 358 times. The dilution of the leather is thus 358. The points so obtained lie approximately on a straight line, and by extrapolation back to logarithm of dilution 0, *i.e.* the dilution represented by the original leather, the *p*H or acid figure is obtained.

In applying this method to paper, the following points need consideration:—(i) the quantities to be taken; (ii) the kind of salt solution, which must be unbuffered and as near to the *p*H of the paper as possible; (iii) the temperature of extraction; (iv) the time required for the attainment of equilibrium in the extraction. It has to be borne in mind that paper should contain little acidity, and that this must not be swamped by the acidity of the salt solution or increased by absorption of acid from the atmosphere.

In preliminary experiments the following *p*H results were obtained after the quantities specified had been allowed to stand for 24 hours in contact with 100 ml. of $M/10$ potassium chloride solution, with occasional shaking:

TABLE II

Weight g.	Light-coloured wrapping paper	Dark-coloured wrapping paper	Filter-paper
1	4·18	4·60	4·76
3	5·26	4·76	4·40
9	5·36	4·66	5·00

The *p*H values should, of course, decrease as the amount of paper used is increased, except in those samples in which the acidity is perfectly buffered. Thus, equilibrium was not attained, and it was concluded that 9 g. of paper was too large a quantity to use with 100 ml. of potassium chloride solution. The following are the *p*H results obtained with less paper and different methods of extraction:

TABLE III

	Light-coloured wrapping paper		Dark-coloured wrapping paper	
Weight g.	24 hours at 18° C.	1 hour's boiling	24 hours at 18° C.	1 hour's boiling
2	5·14	5·14	4·72	4·70
4	5·32	5·14	4·70	4·70
6	5·46	5·14	4·70	4·70

Thus, 24 hours' contact with 100 ml. of $M/10$ potassium chloride solution at 18° C., with occasional shaking, is insufficient for the attainment of equilibrium.

The following table shows the *p*H results obtained by using 100 ml. of $M/10$ potassium chloride solution (*p*H 5·4) and boiling for 1 hour to obtain equilibrium:

TABLE IV

		*p*H of water extract (B.S.I. Method) 2 g. boiled with 100 ml. of water for 5 minutes	*p*H of 100 ml. $N/10$ KCl after boiling the following quantities of paper in it for 1 hour				
Paper	Moisture Per Cent.		2 g.	4 g.	6 g.	*p*H of paper by extra-polation	Approximate *p*H of paper by indicator method
Light-coloured wrapping ..	7·8	5·70	5·14	5·14	5·14	5·14	5·0
Dark-coloured wrapping ..	8·6	4·60	4·70	4·70	4·70	4·70	—
Blotting ..	6·2	3·90	3·85 (3·90)	3·56 (3·64)	3·34 (3·44)	1·0 (1·1)	Much below 3·0
White writing ..	5·7	4·32	4·06	4·02	3·98	3·60	3·7

The following remarks may be made in connection with these results:

(i) The figures in brackets show the effect of using 100 ml. of $M/10$ potassium chloride solution adjusted, for the extraction, to *p*H 7·0 with $N/10$ sodium hydroxide solution.

(ii) In plotting the *p*H values against the logarithms of the dilutions it was found that the three points were practically in a straight line in every instance. This is a useful indication that the results are reasonable.

(iii) There is good agreement between the *p*H values of the paper obtained by this method and the approximate values given by the indicator method.

(iv) These results support Edge's contention, that boiling water does not extract all the acidity from paper.

(v) In order to perfect the details of the method, experiments on the following lines are required:—(*a*) determinations with a large variety of papers, to ensure that the conditions finally chosen suit as many kinds as possible; (*b*) extraction at laboratory temperature in a shaking-machine, to make sure that undesirable changes are not produced by boiling some kinds of paper with $M/10$ potassium chloride solution; (*c*) determinations with a salt solution of the potassium chloride type, but with a *p*H of 6·0–7·0, for papers which are almost acid-free, to make sure that no error is introduced by the use of a solution with a *p*H as low as 5·4; (*d*) de-greasing of waxed or greased papers.

(3) *Method for determining the total amount of acid present in paper.*—The *p*H alone is not a sufficient criterion of quality, because the amount of damage which the paper can do to any article in contact with it must be dependent on the quantity of acid present, as well as its strength or *p*H.

The quantity of alkali required to neutralise the acids in the paper below *p*H 7·0 can probably be determined by a modification of the following method, which was devised by Thompson and Atkin[14]:—Various lots of finely divided leather, each weighing 2·45 g., are placed in resistance-glass flasks or bottles, which are closed with rubber bungs or paraffined corks. To each lot of leather are added 100 ml. of a solution made up of 50 ml. of $M/5$ potassium chloride solution (analytical reagent quality), x ml. of $N/10$ sodium hydroxide solution, and $50-x$ ml. of distilled water, so that the concentration of potassium chloride in each instance is $M/10$. The flasks or bottles are shaken frequently over a period of 48 hours. The *p*H is then determined, preferably with the glass electrode. The *p*H values are plotted as ordinates and the ml. of $N/10$ sodium hydroxide (values of x) as abscissae. The value of x corresponding with *p*H 7·0 is read from the graph, and from this the amount of acid present can be calculated in terms of sulphuric acid, or on any other convenient basis.

(4) *Method for determining the mineral acid content.*—The Procter–Searle[15] method, which was adapted from one used in the analysis of vinegar, has proved valuable for determining mineral acid in vegetable-tanned leather in the absence of materials containing sulphur compounds. The principle of the method is that any mineral or organic acids present are neutralised by the addition of a convenient quantity of $N/10$ sodium carbonate solution. The leather is then destroyed by ignition, and the sodium salts of the organic acids are re-converted into sodium carbonate. Thus, any deficiency of sodium carbonate found on titrating a solution of the ash is due to mineral acids.

In applying this method to paper, 1–2 g. was weighed into a platinum dish, 25 ml. of $N/10$ sodium carbonate solution were added, and the mixture was

evaporated to dryness on the water-bath. The evaporated residue was heated for 15 minutes in an oven at 105° C. to prevent spirting, and the dish was ignited carefully at a dull red heat (500–550° C.) in an electric muffle furnace until ashing was completed. The dish was cooled, 25 ml. of $N/10$ sulphuric acid were added to the residual ash, and the contents were washed into a beaker, so as to give about 100 ml. of solution. This was heated for 15 minutes, and allowed to cool, and the excess of acid was titrated with $N/10$ sodium hydroxide solution, methyl orange or bromophenol blue being used as indicator. The following table gives the results obtained with several papers:

TABLE V

Sample No.	Description of paper	Free mineral acid (calculated as H_2SO_4) Per Cent.
1	Light-coloured, coarse, unsized wrapping paper of low quality	−0·44
2	Dark-coloured, sized wrapping paper of high quality	−0·39
3	Filter-paper	+0·15
4	Blotting paper	−0·20
5	Blotting paper acidified with 0·5 per cent. sulphuric acid	+0·10
6	White writing paper	−0·05

The filter-paper and the acidified blotting paper were the only ones that gave positive results, and therefore probably contained mineral acid. With the other papers the final solution was alkaline instead of acid; it was therefore titrated with $N/10$ sulphuric acid, and the result was calculated as "negative sulphuric acid" to show the amount of acid required to bring it to the neutral point. This frequently happens with protected leathers, and the per cent. of negative sulphuric acid gives an indication of the amount of "buffer salt" (salt of a comparatively weak organic acid) present.

(5) *Method for determining the alkalinity of the ash.*—It might be thought that a paper cannot be acid if it gives an alkaline ash. Thus a quick method of testing a sample would be to dissolve the ash from 5 g. in 50 ml. of $N/10$ hydrochloric acid by boiling for 15 minutes, allowing the solution to cool, and determining the excess of acid by titration to bromophenol blue at *p*H 3·7. Mineral acids and strong organic acids cannot exist in the presence of such substances as calcium carbonate, aluminium oxide or aluminium resinate, but it seems possible for organic acids, which would be strong enough to have harmful effects on metals, for example, to exist in some papers which give an alkaline ash.

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The Determination of Tannins in Cacao Kernel

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I. INTRODUCTION.—The method which has been most widely applied to the determination of tannin in cacao products is that of Chapman,[1] who precipitated the tannin as cinchonine tannate, dried and weighed the precipitate, and calculated a factor for converting the weight into the corresponding amount of tannin. Those methods which involve adsorption or oxidation, *e.g.* the hide powder method, Löwenthal's method, and the iodine method, have the disadvantage that non-tannin substances may be affected, and the final result may vary with the composition of the material investigated. Ainsworth Mitchell[2] surveyed the methods of determining tannins, and pointed out the difficulties in each method. He favours the ferrous tartrate colorimetric method, but with fresh cacao beans the purple pigment in the extract renders colorimetry difficult. On the whole, therefore, Chapman's gravimetric method appears to be the most suitable for cacao beans.

Jensen[3] modified Chapman's method for application to cacao, and his procedure, in outline, is as follows:

Twenty-five g. of cacao nib, 460 ml. of water, and 37 ml. of 0·1 N sodium hydroxide solution are heated for 30 minutes on a boiling water-bath. The gross weight is then made up with water to its previous figure, and the mixture is filtered. Fifty ml. of the filtrate are treated with 150 ml. of saturated cinchonine sulphate solution, allowed to stand for 4 hours or overnight, and filtered through counterpoised papers. The precipitate is dried, first in air and then at 105° C., and weighed, and the weight, multiplied by the factor 0·534, gives the tannin.

McDonald[4] applied Jensen's method to fresh cacao kernel, and concluded from a comparison of the results obtained by Adam[5] and by Jensen, both of whom used the cinchonine method, that the temperature and reaction of the extracting medium are of the utmost importance. McDonald added ammonium acetate to the extracting solution as a buffer, carried out a preliminary titration to find the exact amount of alkali necessary for neutralising the free acids, and carefully standardised the method in order to obtain comparable results. In spite of this, he was not quite satisfied, and advised further investigation of the method.

II. EXAMINATION OF THE CINCHONINE METHOD.—*Effect of pH of the Extracting Medium.*—In order to test the importance of the *p*H of the extracting medium, a sample of fresh Forastero kernel was divided into four 25-g. portions, and extraction was carried out at reactions ranging from *p*H 4·0 to 9·2. The results are shown in Table I.

TABLE I

Weight of kernel g.	Acid or alkali added ml.	*p*H after extraction	Tannin on undried material Per Cent.
25	15 ml. 1 per cent. H_2SO_4	4·00	2·29
25	nil	6·25	2·04
25	25 ml. *N*/10 NaOH	7·30	3·78
25	60 ml. *N*/10 NaOH	9·23	5·73

Thus the *p*H has a marked effect on the amount of cinchonine precipitate obtained, particularly on the alkaline side. It was observed that the precipitate was blue-grey in the acid, and fawn in the alkaline, solutions. This change of colour at reactions above neutrality suggested that different compounds were extracted, but it is not known if these were true tannin bodies. Filtration of the cinchonine precipitate became more difficult with increasing alkalinity, and thus, from the analytical point of view, extraction in slightly acid solution appeared to be preferable, since comparable results could be obtained.

Extraction with water and adjustment of the *p*H with sodium hydroxide or sodium acetate after extraction, gave the results in Table II.

TABLE II

Extract ml.	Sodium hydroxide or acetate added ml.	*p*H immediately before pptn.	Tannin on wet material Per Cent.
50	nil	6·42	2·05
50	25 ml. *N*/10 Na*Ac*	6·58	1·86
50	1 ml. *N*/10 NaOH	7·22	1·52
50	2 ml. *N*/10 NaOH	8·05	1·92

Comparison of Tables I and II shows that the *p*H has a much greater effect during extraction than during precipitation. This may be explained by the fact that a saturated solution of cinchonine sulphate has *p*H about 6, and since, in the precipitation, 150 ml. of this solution were added to 50 ml. of extract, the dominant *p*H was that of the cinchonine sulphate solution.

Extracting Medium.—After extracting fresh kernel with hot water, considerable difficulty was experienced in filtration. "Filtercel" was added, but even this did not entirely overcome the trouble. Fermented kernel samples were even more difficult to deal with, and accordingly it was considered possible that a better extracting agent might be found. Trimble's[6] acetone method was elaborated by Huber,[7] who found that 40 per cent. acetone in water extracts more tannin than water alone, although 100 per cent. acetone extracts no tannin. With regard to the tannin compounds precipitated by cinchonine sulphate, preliminary tests with cacao kernel showed that extraction with 40 per cent. acetone gave approximately the same value as extraction with hot water. It will be seen later, however

(Table III), that better extraction of other phenolic complexes is obtained. Further, the acetone extraction is carried out in the cold—an important point when dealing with readily oxidisable compounds. The acetone extract can be filtered more readily than the aqueous extract, and it is possible to filter, wash, and make the filtrate up to a definite volume, whereas Jensen adjusted his volume *before* filtration.

Extraction with 40 per cent. acetone was carried out for periods ranging from 3 hours to 96 hours, and no appreciable difference in the results was found. In the routine procedure the extraction was carried out overnight.

Filtration of the Cinchonine Tannate Precipitate.—Jensen collected this precipitate on counterpoised filter-papers, but this is unsuitable for the humid tropics, where atmospheric humidity may change from 60 to 90 per cent. within a few minutes. Accordingly, Gooch crucibles were used, but the colloidal nature of the precipitate made it necessary to use a thin layer of coarse asbestos, and to decant as much as possible of the supernatant liquid. Before filtration, the crucibles were washed with half-saturated cinchonine sulphate solution, and dried at 104° C.

III. QUANTITATIVE APPLICATION OF STIASNY'S REACTION.—Stiasny[8] obtained a red precipitate by treating catechol tannins with a mixture of hydrochloric acid and formaldehyde. By standardising the conditions and adding excess of the reagent this reaction could be applied quantitatively to the filtrate from the cinchonine tannate precipitate. Precipitation in the cold was slow and, in order to ensure complete precipitation, the mixture was left standing overnight and then boiled for two hours under an air-condenser. The copious red granular precipitate obtained could be collected without difficulty in a Gooch crucible; it was washed with water, dried at 104° C. and weighed.

In comparative extractions of fermented cacao kernel with water and with 40 per cent. acetone the values in Table III were obtained. The results are calculated on oven-dried material.

TABLE III

1 Method of extraction	2 Cinchonine sulphate tannins (cinchonine tannate × 0·534) Per Cent.	3 Stiasny compounds in filtrate from cinchonine tannate Per Cent.	4 Sum of 2 and 3 Per Cent.
Water, 30 mins. at 98° C.	4·99	3·42	8·41
Cold, 40 per cent. acetone, 3 hrs.	4·84	6·17	11·01
Cold, 40 per cent. acetone, 7 hrs.	4·91	6·25	11·16
Cold, 40 per cent. acetone, 24 hrs.	5·01	6·15	11·16

It is evident that 40 per cent. acetone extracts more of the compounds which are precipitated by the acid-aldehyde mixture than does water, the proportionate difference being reasonably near the figure given by Huber,[7] who stated that the amount extracted by water is 80 per cent. of that extracted by 40 per cent. acetone.

Stiasny's Reaction on Original Extract.—The quantitative Stiasny reaction was also applied to the acetone extract before precipitation with cinchonine sulphate. The percentage thus obtained was in every instance approximately equal to the sum of the percentage of tannin by the cinchonine method (*i.e.* cinchonine tannate $\times 0{\cdot}534$), plus the percentage of Stiasny compounds in the filtrate from the cinchonine tannate. This point will be considered later (Table IV).

IV. Method Finally Adopted.—(1) *Extraction.*—Twenty-five g. of kernels (either fresh or fermented), which have been passed through a mincing machine, are extracted overnight in 220 ml. of cold 40 per cent. acetone. The extract is filtered through a 10·5-cm. Buchner funnel with a No. 41 Whatman paper which has been pre-coated with 2 g. of kieselghur (or other filter-aid). The residue is washed with 20 ml. of 40 per cent. acetone, and the filtrate is made up to 250 ml. with water.

(2) *Cinchonine Precipitate.*—Triplicate 25-ml. portions of the extract are each treated with 150 ml. of saturated cinchonine sulphate solution, left standing for 5 hours (or overnight), *decanted* on to a Gooch crucible having a pad of *coarse* asbestos which has been washed with half-saturated cinchonine sulphate, dried at 104° C. and weighed. The cinchonine tannate precipitate is washed with half-saturated cinchonine sulphate solution, dried overnight in a sulphuric acid desiccator, oven-dried at 104° C., and weighed. The weight of the precipitate, multiplied by 0·534, gives the weight of tannin. The filtrate is retained for further treatment (see (4)).

(3) *Stiasny's Reaction.*—Duplicate 25-ml. aliquot portions of the extract are left overnight in 300-ml. conical flasks with 25 ml. of water and 25 ml. of a hydrochloric acid and formalin reagent (100 ml. of conc. HCl, 100 ml. of water, 150 ml. of 40 per cent. formaldehyde). The mixture is boiled under an air-condenser for one hour, and the precipitate is filtered off on a weighed asbestos Gooch crucible, dried at 104° C. and weighed.

(4) *Stiasny's Reaction on the Filtrate from Cinchonine Tannate Precipitate.*—The filtrate from (2) is left standing overnight with 50 ml. of hydrochloric acid and formalin mixture, and then boiled under an air-condenser for one hour, and the precipitate is filtered off, dried at 104° C., and weighed.

V. Analytical Data.—Table IV gives some results obtained by the method outlined above. The results are expressed as percentages on oven-dried material.

Table IV

1	2	3	4	5
Type of beans	Tannin by cinchonine sulphate method Per Cent.	Stiasny compounds in filtrate from cinchonine tannate Per Cent.	Sum of 2 and 3 Per Cent.	Stiasny compounds in original extract Per Cent.
Fresh Forastero	3·39	4·88	8·27	8·88
Fermented Forastero	3·69	0·39	4·08	4·93
Unfermented Forastero	4·47	3·79	8·25	9·43
Fresh Criollo	3·26	4·52	7·78	8·30
Fermented Criollo	3·59	0·64	4·23	5·60

The striking feature in Table IV is the diminution, due to fermentation, of the Stiasny compounds in the filtrate from the cinchonine tannate precipitate. It is probable that this is a measure of catechin and similar phenolic compounds, since Adam [5] found that catechin disappears on fermentation. Hooper[9] suggested that cinchonine sulphate may have special value in determining tannin in the presence of catechin, and it is possible, therefore, that Chapman's method, as applied here, determines only the tannins. The complete method described above may thus serve to distinguish between true tannins and other phenolic substances, such as catechin. The chief technical difficulty in the procedure lies in the filtration of the cinchonine tannate precipitate, but in extreme instances it would be possible to obtain the same figures without weighing the cinchonine tannate precipitate. The reasonable agreement of the sum of the two fractions with the formaldehyde-acid precipitate on the original extract allows the alternative of filtering off the cinchonine tannate on a coarse filter-paper or by other rapid means, discarding this precipitate, and using the difference between the two results by the Stiasny reaction as a measure of the cinchonine sulphate tannins.

SUMMARY.—1. Chapman's cinchonine sulphate method for determining tannin was investigated with regard to its application to fresh and fermented cacao beans.

2. Cold 40 per cent. acetone was found to be a better extracting agent than hot water, and extraction overnight was adopted as a routine procedure.

3. Stiasny's reaction for catechol tannins, *i.e.* precipitation with a mixture of formaldehyde solution and hydrochloric acid, was applied quantitatively, and gave consistent results.

4. The filtrate from the cinchonine tannate precipitate gave a precipitate by Stiasny's method, and it is suggested that this may be a measure of the catechin and similar phenolic compounds, for the value obtained decreases markedly when beans are fermented.

5. On applying Stiasny's reaction to a 40 per cent. acetone extract of fresh or fermented cacao beans, the figure obtained was in agreement with the sum of the tannin precipitated as cinchonine sulphate and the Stiasny precipitate obtained from filtrate.

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The Determination of Sodium in Aluminium and Aluminium-Silicon Alloys

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A. C. COATES, B.Sc., A.I.C.

Introduction.—The amount of sodium present as a minor impurity in aluminium and aluminium-silicon alloys has always been of interest to producers of this metal. It is probable that originally this interest arose out of the relatively poor quality of the aluminium obtained by direct chemical reduction. To-day the main interest centres round aluminium-silicon alloys of the type first developed by Pacz, in which sodium or certain sodium salts are specifically used as modifying agents for the refinement of the grain structure. The electrolytic reduction process for the production of aluminium has been so improved that present-day commercial aluminium is of a high degree of purity so that only minute amounts of sodium are present in the metal (0·001 to 0·008 per cent.). In the aluminium-silicon alloys mentioned above the sodium-content is appreciably greater and may vary from 0·005 to 0·04 per cent.

The determination of sodium in aluminium has always presented difficulties, and much time has been spent by many workers in an endeavour to find a process that was accurate. As long ago as 1859 St. Claire Deville worked out a method for the determination of sodium in aluminium, in which he converted the aluminium into nitrate, ignited at a low temperature, and then leached out the alkalis with water.[1] Many later workers[2,3,4,5,6,7,8,9,10,11,12,13] have used the same method with various modifications, but none has proved really satisfactory. From time to time other methods have been put forward,[14,15,16,17,18,19,20,22] but of all the methods that we have examined the best has undoubtedly been that devised by Fairlie and Brook.[21] This method, which depends on the removal of the aluminium from solution by crystallisation of aluminium nitrate and the determination of the sodium as sulphate in the filtered liquid, has been in operation for the last ten years on a semi-routine basis. Under the best conditions it has been found possible for routine workers to carry out five determinations in two days, and in the hands of a person skilled in the method very accurate results have been obtained. It obviously left much to be desired when considered as a routine process, and when the demand for aluminium-silicon alloys increased, it became imperative for a more rapid method to be developed, even at the sacrifice of a little accuracy.

In 1932 Bridges and Lee[23] published what they called a "fusion leach" method, which seemed to be very much simpler and more rapid than any method previously suggested. It has the obvious advantage that, whilst large quantities of sample could be used (50 to 70 g.), the complications of separating the aluminium from the sodium chemically were eliminated, and the figures reported in the paper indicated reasonable accuracy. Almost simultaneously with the publication of that paper another worker, Scheuer,[24] published details of a similar method, which

showed the same advantages of simplicity and speed. The obvious possibilities of such a method led the authors to make a further investigation of the principle, using Scheuer's work as a basis. As a result, the Scheuer method has been developed and improved, so that it may be safely used as a routine control process.

PRINCIPLE OF THE METHOD.—The method depends on the fact that when aluminium is maintained in a molten condition at about 900° C., the sodium is released and becomes oxidised at the surface. After cooling, the metal is washed with hot water, and the alkaline solution so obtained is titrated with standard acid.

APPARATUS.—The furnace designed for the heating of the aluminium samples is shown in Figs. 1 and 2.

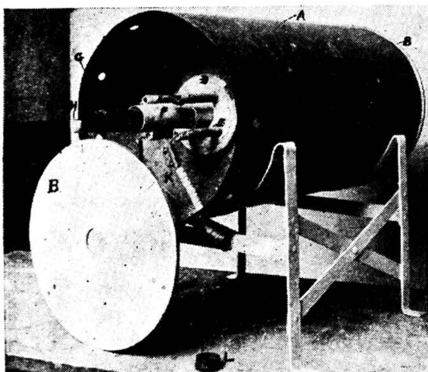
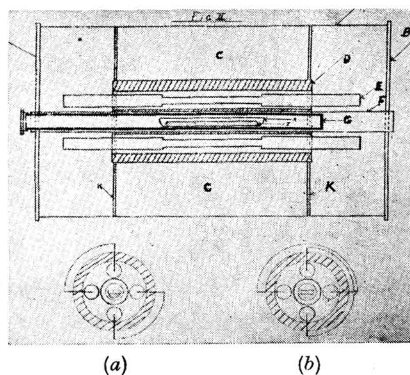


Fig. 1.

A. Metal casing
B. Detachable ends of furnace
C. Heat-insulating material
D. Sillimanite tube
E. Silit rods
F. Cronite tube
G. Iron combustion tube (calorised)
H. Iron boat
K. Circular supports
L. Loose-fitting cap for combustion tube



(a) (b)

Fig. 2.

A. Metal casing
B. Detachable ends of furnace
C. Heat-insulating material
D. Sillimanite tube
E. Silit rods (heating elements)
F. Cronite tube
G. Iron combustion tube (calorised)
H. Iron boat
J. Aluminium sample
K. Circular supports

Fig. 1 represents a photograph of a single-tube furnace (a double-tube furnace is now used, as this affords saving in both time and electrical energy where large batches of samples require to be handled).

Fig. 2 shows in diagrammatic form the construction of the furnace. It consists essentially of a cylindrical sillimanite or alundum tube, 4 in. in internal and 5 in. in external diameter, and 12 in. long, carrying two plugs of similar material (one at each end); these have four holes symmetrically placed to carry heating elements. In the centre of each end-piece is a hole, $1\frac{5}{8}$ in. in diameter, through which a Cronite tube, 14 in. long and $1\frac{3}{8}$ in. in internal diameter is fixed.*

* Cronite tubes may be obtained from the Cronite Foundry Company, Ltd., Lawrence Road, Tottenham, N.15, price 25s. each.

The sillimanite tube is suitably mounted and efficiently lagged with asbestos, and the whole is enclosed in a sheet-iron casing. The furnace is heated by means of the four Silit* rods connected as two parallel pairs in series. The inner Cronite tube carries an iron combustion tube, 18 in. long, by $1\frac{1}{16}$ in. internal and $1\frac{1}{4}$ in. external diameter, closed at one end and provided with a loosely-fitting cap at the other. This iron tube carries, in turn, an iron boat, 8 in. long, of semicircular section, $\frac{7}{8}$ in. external diameter, which holds the sample to be tested.

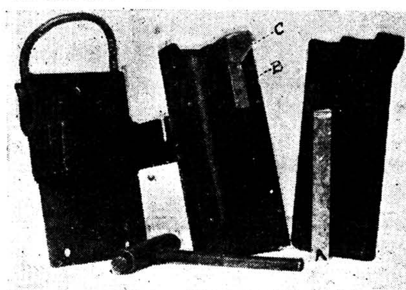


Fig. 3.
Details of half-round chill mould
A. Large chill bar (6 in. long by 1 in. diameter
B. Small chill bar ($1\frac{1}{2}$ in. long by 1 in. diameter
C. Feed head (which is cut off)

Some difficulty was experienced with the iron tubes, which scaled badly during the tests, but this was ultimately overcome by having them calorised. The furnace is worked on a 250-volt D.C. circuit through an adjustable resistance, and the current is regulated so as to give a steady temperature of 900° C. inside the combustion tube.

PROCEDURE.—The metal sample, a solid piece,† 10 cm. long by 2 cm. wide, weighing about 60 g., is carefully freed from its cast skin by milling and filing. The boat and iron tube are washed with distilled water until free from alkali and dried before the sample is placed in the boat. The boat containing the sample is then inserted in the iron tube, which is put into the pre-heated Cronite tube (the temperature inside the tube is 900° C.). The cap is placed on the open end of the combustion tube and the whole left in the furnace for 30 minutes. At the end of this period the iron tube is withdrawn and cooled down in the air to room temperature; this takes about 30 minutes. The boat and aluminium sample are carefully washed with water into a beaker until the wash-water is no longer alkaline. (The metal must be actually removed from the boat for this purpose.) A few drops of 0·6 per cent. Sofnol No. 2 Indicator are added to the solution, and the alkalinity is titrated with $N/100$ hydrochloric acid.

Except in one or two isolated instances when the sodium-content was unusually high, it was found that only negligible amounts of sodium remained on the walls of the combustion tube, and it was therefore unnecessary to wash this tube after each test. The whole of the alkalinity appeared on the surface of the sample and boat.

RESULTS.—In Table I comparative results obtained by the fusion process and by the Fairlie–Brook nitric acid method with various types of metal are shown.

* Silit is a material made by exposing a mixture of silicon, silicon carbide and carbon to the action of carbon monoxide at 1500° C.

† NOTE.—Where molten metal is available, the samples can be readily prepared by casting in a half-round chill mould. This ensures that the samples are of approximately the same size and weight; they are then easily filed. The form of the mould is such as to ensure that the sample fits freely into the boat (see Fig. 3).

TABLE I

SODIUM CONTENT OF ALUMINIUM AND Al/Si ALLOYS

COMPARATIVE FIGURES BY THE FUSION AND NITRIC ACID PROCESSES

Expt. No.	Description	Sodium: Fusion method Per Cent.	Sodium: Nitric acid method Per Cent.
1	Reduction furnace metal for billet cast	0·006	0·006
2	,, ,, ,, ,, ,, ,,	0·004	0·003
3	,, ,, ,, ,, ,, ,,	0·005	0·005
4	,, ,, ,, ,, rolling ,,	0·004	0·003
5	,, ,, ,, ,, ,, ,,	0·003	0·004
6	,, ,, ,, ,, ,, ,,	0·003	0·003
7	Refined metal. Billet cast	0·001	0·002
8	,, ,, ,, ,,	0·0008	0·001
9	,, ,, ,, ,,	0·0006	0·001
10	,, ,, for rolling cast	0·001	0·002
11	,, ,, ,, ,, ,,	0·0005	0·002
12	,, ,, ,, ,, ,,	0·0003	0·001
13	Aluminium silicon alloy	0·023	0·022
14	,, ,, ,,	0·013	0·010
15	,, ,, ,,	0·012	0·010
16	,, ,, ,,	0·010	0·011
17	,, ,, ,,	0·008	0·009

DISCUSSION.—The results shown in Table I are typical of the thousands already obtained by the fusion process. The agreement between the two sets of figures is very satisfactory and indicates that the accuracy of the fusion process is at least equal to that of the chemical method.

As regards the reproducibility of the figures, repeated experiments have shown this to be excellent, the agreement being well within 0·001 per cent. on the pure metal. With silicon alloy the results are not quite so reproducible, but even so, the divergence is frequently no greater than 0·001 per cent. and has never been found greater than 0·003 per cent. on a 0·015 per cent. sodium-content.

In order to obtain consistent figures it is essential that the worker should adhere to the exact conditions of the test for the duration of heating and the temperature. Prolonged heating, or too high a temperature, tends to give low results.

When the test is carried out as described, it has been found that re-heating of the metal for an additional half-hour gives only a very slight further amount of sodium, much less than 0·001 per cent. on a sample containing 0·01 per cent. of sodium. In conclusion, we have no hesitation in recommending this process, in view of its satisfactory operation during the last three years.

We desire to acknowledge our indebtedness to the Directors of the British Aluminium Company, Ltd., for permission to publish this paper.

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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.

THE DETERMINATION OF ORPIMENT IN SHELLAC

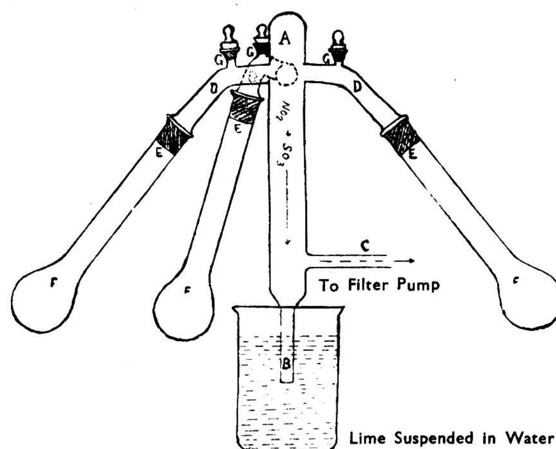
Shellacs usually contain from 0·1 to 0·3 per cent. of orpiment, but occasionally samples containing as much as 0·8 to 1 per cent. are met with. The orpiment is added to impart a lighter colour, but it has an injurious effect on the properties of a shellac film, and is also objectionable owing to its possible poisonous effects when the shellac is used for lacquering tins in the food-canning industry.

The official method of the United States Shellac Association for the determination of orpiment in shellac is tedious, and a modification of the iodimetric method of the Association of Official Agricultural Chemists is more rapid and convenient. The following semi-micro method, which has been based on the iodimetric method, is rapid and avoids the liberation of fumes.

The apparatus consists of a stout, vertical Pyrex glass tube closed at the top and drawn out at the other end to a narrow tube. A little above the narrow end is a side-tubulure connected with an ordinary filter-pump. A few inches below the top end are fused three horizontal tubes, bent downwards at an angle of 120°, and having their other ends widened and provided with ground-glass joints, to fit into the necks of three 100-ml. Pyrex Kjeldahl flasks. Each of the bent tubes has a ground-glass stopper, after removal of which successive quantities of nitric acid can be introduced into the apparatus without disconnecting the flasks. The narrow end of the vertical tube dips into water containing lime or other alkali to absorb any fumes not withdrawn by suction.

A representative sample 25 to 50 g., of the shellac is powdered to pass a 100-mesh sieve, and then, by successive subdivision and mixing, a representative sample of about 5 g. is ultimately obtained. Triplicate portions (0·5 to 1 g.) are weighed out into the three digestion flasks of the apparatus, and each is treated with 2 to 3 ml. of pure (arsenic-free) sulphuric acid. After a short time a few ml.

of conc. nitric acid are added, and each flask is shaken until nitrous fumes are no longer evolved. The flasks are then connected with the apparatus and supported on retort-rings and wire gauze. They are heated, gently at first and then more vigorously, while suction is meanwhile applied. When white fumes of sulphur trioxide appear heating is momentarily suspended, the glass stoppers of the tubes are withdrawn, and 10 ml. of nitric acid are slowly introduced through the openings of the three flasks. Heating is continued, after further additions of nitric acid if necessary, until all organic matter has been oxidised.



The residual nitric acid is expelled by boiling, a few fragments of pumice being introduced to prevent bumping. The flasks are then disconnected, the solution in each is diluted to about 50 ml., the arsenic (now present as arsenic pentoxide) is reduced to the arsenious condition by means of a small crystal of potassium iodide, and the liberated iodine is expelled by boiling until the solution is pale yellow. The solution is again diluted to about half the volume of the flask, and the residual colour of the iodine is *just* discharged by adding $N/100$ sodium thiosulphate (starch solution as indicator). The solution is immediately neutralised by the gradual addition of sodium bicarbonate until an excess of 2 to 3 g. of that salt is present, and titrated with $N/100$ iodine solution, 2 to 3 ml. of freshly-made 1 per cent. starch solution being used as indicator.

To test the accuracy of the method, several determinations were made on samples of commercial shellac and on mixtures of pure shellac with known quantities of orpiment. With mixtures containing 0·93 per cent. of orpiment, the amounts found ranged from 0·91 to 0·93 per cent., and with mixtures containing 0·20 per cent. of orpiment, the results ranged from 0·19 to 0·22 per cent.

For samples containing less than 0·1 per cent. the following modification is recommended:—Five g. of the representative sample are dissolved in 100 to 125 ml. of 95 per cent. alcohol on a water-bath, and the solution is filtered through a filter-paper in a hot-water funnel, the stem of which is fitted into a Buchner funnel connected with a filter-pump. The filter-paper containing the orpiment and other impurities, is folded, dried and introduced into the digestion flask of the apparatus for further treatment as described above.

The apparatus is also suitable for the digestion of small amounts of organic material for the determination of nitrogen by Kjeldahl's method; no fume cupboard is required.

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Report on the Eleventh World's Dairy Congress, 1937

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who represented the Society at the Congress

(*Presented at the Meeting, November* 3, 1937)

This Congress was held in Berlin from August 22nd to 28th, 1937. Over 3700 delegates, from 52 countries, attended the Congress and 414 papers were submitted to the Conference. These papers dealt with the various subjects of the four sections into which the Congress business was divided. The sections comprised: (*a*) Milk production and general dairying; (*b*) the utilisation of milk and the manufacture of milk products; (*c*) legislation, marketing and dairy education; (*d*) dairy engineering, use of power, dairy plant. These sections were further divided into topics, 21 in all, to which workers from different countries were asked to contribute beforehand. The papers on each topic were summarised by reporters. The Conference business consisted of communicating these summaries followed by a short discussion, each topic being disposed of in 90 minutes. It was felt that this was far too short for some important topics, but the volume of material submitted demanded this curtailed treatment. Telephonic communication to each seat enabled the proceedings of meetings to be carried on in three languages (English, French and German) simultaneously.

For descriptive purposes the Congress can be divided into three divisions: (*a*) the Conference, (*b*) the excursions, and (*c*) the International Dairy Exposition.

The Conference.—The accuracy of the application of milk-testing from the standpoint of breeding and feeding was discussed. It was agreed, amongst other matters, that due attention should be paid not only to the correct interpretation of the enormous number of milk samples analysed, but also to other factors entering into the performance of the cow, such as constitution, health and fecundity. Much attention was paid to the economic use of home-grown foodstuffs for milk production during all the seasons of the year, especially the making of silage, the value of winter-green crops, and the use of by-products of the sugar, starch and fermentation industries. The value of young grass in the fresh and preserved state continued to be realised. Clean milk production was discussed, due regard being given to costs of renovation of cowsheds and the returns obtained in healthier stock, and payment for milk on a quality basis. The universal prevalence of various diseases of dairy cows, which interfere with normal milk production and which modify the behaviour of milk in the manufacture of products, was realised, and methods of prevention, control and eradication were discussed. In discussing tropical dairying, the lack of balance between the intensities of population and milk production in various parts of the world was stressed. The seemingly irrational practice of transporting large quantities of dairy products from one temperate zone to another was pointed out.

The significance of abnormal milk, from a scientific and practical standpoint, was adequately treated. Milk low in solids-not-fat, the causes of oily and fishy flavour, and hormonal control of milk composition were described. The compositions of milk produced under conditions when four recognised causes of abnormality obtained (mastitis, end of lactation, drought and persistently low performance) were discussed. The mechanism of the development of a fishy taint in milk through feeding betaine-containing products was dealt with.

Butter problems, such as aroma production and keeping quality, aroused much interest. Knowledge on butter aroma production has advanced considerably

during the last three years, and 14 papers dealing with this topic were submitted. It was generally agreed that diacetyl was mainly responsible for flavour and aroma, and that by the controlled use of butter cultures, these properties could be conferred, in varying degrees, on butter. In butter cultures, diacetyl is formed, when oxygen is present, from acetoin, which under anaerobic conditions is formed in considerable amounts especially by bacteria capable of fermenting citric acid. The formation of diacetyl by the oxidation of acetoin in butter after churning was also established. The method recommended as the best for the determination of diacetyl, or diacetyl plus acetoin was a modification of Barnicoat's method (ANALYST, 1935, **60**, 653). The acidity and bacterial activity of the aqueous phase of butter appears to be most important in defining the storage properties. An acid serum (pH $< 6{\cdot}4$) gives a low storage quality, mostly due to attendant small changes in the butter-fat, such as an increase of organic acidity. Acidity and contamination with heavy metals mostly cause off-flavours owing to oxidation of butter-fat. No important new methods of following fat-oxidation were offered for discussion. Pasteurisation of milk for cheese-making, mostly by the flash method, was found in every instance to improve quality, but sometimes to lengthen the ripening period. In addition to killing pathogenic organisms, pasteurisation enables the development of acidity in the milk, by addition of a specific starter, and the ripening process to be more adequately controlled. Much of the work, however, was done on cheese of local importance only, and reports on cheese which account for a greater portion of the world's supply would have been welcomed.

The utilisation of surplus milk and liquid by-products was treated only on general lines, and there was nothing new reported in addition to the various avenues of disposal which have been in the minds of dairy technologists for the last 15 years. The main features in solving the problem rest on the increased use of dried or condensed by-products in food technology and the financial returns accruing from products of lower nutritive value than milk or its main products.

Control and improvement of the quality of milk and its products go hand in hand. The parts played by State and private measures in this direction were fully discussed. The importance of uniform methods of grading, the holding of competitions and the appreciation, by the buying public, of efforts towards improvement of quality were stressed. Standards of quality enforced in various countries, the enforcement of these regulations, methods of assessing quality, and payment on a quality basis were discussed.

Of importance to analysts were the resolutions passed concerning the standardisation of methods of analysis of milk powder and processed cheese. The International Dairy Federation (which is the body sponsoring the Dairy Congress) had already, in 1934, adopted *in toto* the methods of this Society for the analysis of condensed milks.* In 1936, the Federation agreed that this Society's methods for the analysis of milk-powder should also be adopted. These methods, of course, are not enforced as industrial control methods, but would be used in cases of international differences of opinion. The resolutions embraced the terminology—milk-powder or dried milk—limits of composition (namely, not more than 6 per cent. of moisture and not less than 24 per cent. of fat in whole milk-powder), and the description of the contents of the package (namely, net weight and "milk powder containing A per cent. of fat").

The resolutions with regard to processed cheese were: (*a*) there should be only one designation for processed cheese in every country, (*b*) fat-standards should be fixed, (*c*) the amount of emulsifying salts should not exceed 3 per cent. of the product. Other topics dealt with included the economics of milk distribution and

* The International Dairy Federation has not yet published these methods, although the Society's methods, in English, French and German, were circulated among the members of the Federation at the time of the Congress.—EDITOR.

sales; the methods employed for the production of hygienic milk in various countries; the organisation of dairy plants and dairy education.

A considerable number of papers were submitted dealing with the nutritive value of milk. Few dealt with research on the subject; most were concerned with means adopted for popularising the sale of milk and its products. Variations due to breed of cow, feeding, and methods of handling were discussed.

In the power and engineering section, the planning of dairies, the disposal of sewage, economy of power, and the development of dairy machinery for which modern alloys are used were discussed. It has been found practicable to dispose of dairy sewage by biological oxidation in percolating filters or by certain modifications of the activated sludge process. The question of "milk and metals" was again brought up; the behaviour of modern alloys towards detergents and acid milk products, and the importance of the heat conductivity of metals, resulting from recent developments in connection with heat exchange were discussed.

EXCURSIONS.—Opportunities were offered for afternoon trips to centres of interest during the Congress and long-period study trips to various parts of Germany afterwards. A visit to the Berlin municipal sewage farm showed intensive irrigation of land with clarified sewage, the grass being fed indoors for milk-production. The farm was an example of the German "campaign against waste." The milk-processing depots were efficient and practically planned. Almost all milk was flash-pasteurised and holder pasteurisation was almost unknown. Produce-storage depots controlled quality rigidly, this being a great factor in improving public appreciation of food of good quality. The Berlin research laboratories were well equipped and staffed, and primary education in food and dairy science was thorough. The longer excursions gave an opportunity of studying German methods of cattle-breeding and milk-production, of visiting dairy schools, manufacturing depots and research institutes, and of gaining a knowledge of German dairying generally.

THE INTERNATIONAL EXPOSITION.—This was housed in five halls at Witzleben. This innovation for the Congress was a pronounced success, both to exhibitors and delegates. The machinery hall was packed with the newest plant from every participating country. Scientific apparatus was shown here to advantage; one improvement, exhibited by both Funke and Gerber, consisted in methods for filling 24 to 36 Gerber tubes with acid simultaneously. Methods of dairy education and propaganda in use in various countries were shown. International competitions in fresh and stored butter proved instructive, and the display of cheese types was comprehensive. The value of combining an exhibition of this scope with the ordinary Congress business was thoroughly appreciated.

NATIONAL INSTITUTE FOR
RESEARCH IN DAIRYING
READING

Official Appointment

THE Minister of Health has approved the following appointment:

JOHN ROBERT STUBBS as a Public Analyst for the County of Lancashire, in place of G. D. Elsdon (resigned) (November 16th, 1937).

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 would be submitted to the Publication Committee.

CITY OF BIRMINGHAM

Reports of the City Analyst for the Second and Third Quarters, 1937

In the Second Quarter 75 of the 1373 samples, and in the Third Quarter 34 of the 1426 samples, were bought formally.

Soda-mint Tablets.—One sample, although containing the correct amount of sodium bicarbonate, contained no ammonium bicarbonate, which is included in the B.P. Codex formula. The vendors stated that they only supplied the B.P.C. article when ordered on a prescription, or when asked for as soda-mint tablets B.P.C., and suggested that they might label the non-official tablets "Soda-mint Tablets, Old Style," since they were made from a formula in existence before the Codex adopted the term "Soda-mint" as a synonym for "Tab. Sodium Bicarb. Co." They were advised, however, that this would still be regarded as a contravention of the labelling section of the Food and Drugs Act. For the present, the shop concerned has been instructed to supply the Codex article when soda-mints are asked for.

Formalin Tablets.—In the B.P. Codex the terms "Formalin Throat Tablets" and "Formamint Tablets" are allowed as synonyms. Samples bought under the first of these synonyms should have contained 9·7 mg. of paraformaldehyde in each tablet, whereas one sample contained only 4 mg. The pharmacist concerned was informed by his suppliers that the tablets were made to their own formula. In future he will specify "B.P.C. tablets" when ordering them.

China Tea "Practically Free from Tannin."—A sample bearing this label contained 8·6 per cent. of tannin, which is a normal figure for China tea. The packers wrote that, in their opinion, the quantity of tannin in a pound was so small, compared with that in Indian or Ceylon tea, that they thought the phrase "practically free from tannin" was a fair description. They agreed to omit the words in future, and were allowed three months to exhaust their stock of labels.

Malted Milk.—This article should consist entirely of a mixture of dried milk and malt extract. One sample, however, contained no less than 23 per cent. of cane sugar. The stores from which it was purchased had a warranty from their wholesale dealers, who got into touch with the Department on hearing of the trouble. They were informed that if they altered the labelling of their malted milk by the addition of words indicating that it contained cane sugar, it would, so far as Birmingham was concerned, be in order. They were also, however, reminded of Subsection 2*a* of Section 2, of the Food and Drugs (Adulteration) Act, 1928, which implies that an offence is committed if a substance is added to a food or drug so as to "fraudulently increase the bulk, weight or measure, or to conceal the inferior quality thereof." There must, of course, come a point at which the addition of a substance, such as cane sugar, to malted milk becomes fraudulent, even though the fact of the addition be mentioned on the label. It could not be held, for instance, that the phrase "Contains added cane sugar" would cover a mixture of 25 per cent. of malted milk and 75 per cent. of sugar.

Blue Pills.—The pill mass from which these are made should contain 33 per cent. of metallic mercury. Two samples of 2-grain pills from the same shop were deficient in mercury, containing only 26 per cent. In addition to the shortage of mercury, the pills were badly made, the coating being not adherent,

but present as a loose powder in the box. The weights of the pills showed an excessive variation—from 1·75 to 2·3 grains. The pharmacist concerned had his pill mass examined by an independent analyst and also analysed it himself. The results showed that the correct percentage of mercury was present, and that, therefore, the deficiency in the pills sold was due to their being made hurriedly and to the use of some excipient in the process. The variation in weight was explained by uneven rolling, which should not have occurred had more time been taken in making the pills. The assistant responsible for the work had left.

Two other samples proved on analysis to be, not blue pills, but calomel pills. An investigation was made by the firm, and all the stock was withdrawn from sale.

H. H. BAGNALL

CITY OF MADRAS

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1936

THE Madras Prevention of Adulteration Act, 1918, is slowly having a beneficial effect upon the quality of foods sold in the City. The percentage of adulterated samples in 1936 was 23·9, compared with 32·9 in 1935 and 35·7 in 1934. The 1028 samples examined during the year included 523 of ghee, 246 of gingelly oil, 98 of butter, 74 of milk, and 62 of ground-nut oil.

ADULTERATION OF GHEE.—Adulteration of ghee with foreign fats was forbidden by G.O. No. 3081, Public Health, dated November 28th, 1935, and the value of this rule was reflected in the fall in the percentage of adulterated samples from 44·4 to 28·9. The common adulterants were hydrogenated oils in proportions ranging from 10 to 95 per cent.

GINGELLY OIL.—Only 5·3 per cent. of the samples were adulterated. In every instance the adulterant was ground-nut oil in proportion ranging from 10 per cent. to complete substitution.

GROUND-NUT OIL.—Of the 23 adulterated samples, 7 were pure gingelly oil, 15 were mixtures of ground-nut and gingelly oils, and 1 contained 10 per cent. of coconut oil.

V. VENKATACHALAM

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

LEMON SYRUP

ON November 25th a firm of druggists was summoned by the Wolverhampton Corporation for selling lemon syrup alleged to be deficient in lemon juice.

Mr. S. M. Gore appeared for the prosecution, and the defendants were represented by Mr. R. Parry.

Mr. Gore said that the sample of syrup in question had been analysed and found to consist of a flavoured solution of sugar artificially coloured. In his submission the ordinary purchaser of lemon syrup would expect to get an extract from the whole of the lemon and not merely oil from the peel.

Mr. F. G. D. Chalmers, Public Analyst for Wolverhampton, said that he would expect to find 30 per cent. of lemon juice in lemon syrup.

Mr. A. F. Lerrigo, Public Analyst for Birmingham, said that, in his opinion, lemon syrup should contain from 25 to 30 per cent. of lemon juice.

Dr. E. J. Parry, giving evidence for the defence, said that the lemon syrup condemned in this case was genuine, and similar to 90 per cent. of the lemon syrup of this character sold in this country. It was about twice as strong as the standard in the British Pharmacopoeia. Lemon juice was particularly liable to ferment, and it was therefore exceptional to find it in a lemon syrup preparation.

Mr. R. Parry called several technical witnesses for the defence. He stated that the syrup had been sold for years without challenge.

The Stipendiary said that he had not formed a final decision as to how lemon syrup should be sold, and in future cases he might be influenced by the labels used by vendors. He was satisfied that there had not been a breach of the Food and Drugs Act, and therefore dismissed the case.

Fifteen guineas costs were awarded against the Corporation.

Report of the Government Chemist upon the Work of the Laboratory

FOR THE YEAR ENDING 31ST MARCH, 1937*

THE chemical work during the year has been done on behalf of the same Government Departments as formerly (see ANALYST, 1936, **61**, 841), mainly at the Laboratory at Clements Inn Passage. The Custom House Laboratory deals specially with Customs samples, and the Chemical Stations, in various parts of the country, with some Customs and Excise samples. There are additional laboratories at the Geological Survey Museum, Park Royal and Deptford. The total number of samples examined during the year was 545,261, a decrease of 1018 on those of the previous year. The samples of tea show a decrease of 10,000 (last year's figures were abnormal owing to wharf fires); sugar samples decreased by 6000, but tobacco samples increased by 7000, and samples of silk, spirits, cocoa, wine, and import duty samples all show increases.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter and Margarine.*—Of 848 samples of butter, one contained 0·05 per cent. of boric acid, and of 48 samples of margarine one contained over 16 per cent. of water. The samples of margarine have decreased still further in number this year, owing to decreased imports.

Cheese.—No samples contained foreign fat.

Cream.—The fat in 90 samples ranged from 19 to 76·4 per cent.

Sheep Dips.—Of 89 samples submitted, 15 would not have satisfied the Regulations, when prepared as directed.

Sea Water.—In accordance with the Oceanic Research Scheme as described in last year's report the salt concentration was taken in 6139 samples, and 155 samples of sea-water were examined for the proportion of dissolved oxygen present.

Water Pollution of Rivers.—The samples of river water (91) were examined from the point of view of fish-life, and 8 samples of proprietary road dressings for the presence of substances harmful or toxic to fish.

Fertilisers and Feeding Stuffs Act, 1926.—Two fertilisers and 7 feeding stuffs were examined. A lawn fertiliser was deficient in nitrogen and contained an excess of insoluble phosphoric acid, and required particulars were not correctly given. "Kainit" contained only 0·14 per cent. of K_2O. Of 4 ground-oat samples, all contained foreign cereals, but in one instance the amount was sufficiently small for the sample to be regarded as produced from oats as grown. The remaining feeding stuffs showed deficiencies in oil or albuminoids, or both. In every instance,

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 9d. net.

except in the proportion of foreign matter in one of the ground-oat samples, the results confirmed the findings of the agricultural analysts concerned.

Agricultural Produce (Grading and Marking) Acts. National Mark Schemes.—The 365 samples of flour included 21 marked Yeoman; 3 samples of malt, and malt extract and cod-liver oil, 261 of cider, 8 of perry, and 87 of honey were examined under the various regulations. The regulations provide for 2 grades of Cheshire cheese, 3 grades of Stilton, 2 grades of Cheddar, and one grade each of Caerphilly, Lancashire, Wensleydale, Leicester and Derby cheese, with not less than 45 per cent. of butter-fat. All these grades must contain not less than 45 per cent. of butter-fat in the dry substance, excepting one grade of Stilton with a minimum of 50 per cent. There are also 2 grades of cream cheese with not less than 70 and 55 per cent. respectively of butter-fat in the cheese. The samples of cheese examined numbered 472, including 142 Cheshire, 148 Stilton, 17 Cheddar, 12 cream, 50 Caerphilly, 72 Lancashire, 27 Wensleydale, 5 Leicester, and 2 Derby.

Ninety-three samples of water from watercress intakes and beds were examined chemically and bacteriologically. Miscellaneous samples included 5 insecticidal preparations in connection with spraying potatoes against Colorado beetle, and 8 samples of derris preparations in connection with the Warble Fly (Dressing of Cattle) Order, 1936.

CUSTOMS AND EXCISE.—*Beer.*—Of the total 47,796 samples examined, most were tested to determine the original gravity of the beer. Of 4141 samples of wort, 101 were found to be under-declared, and in 19 of 614 samples of beer there was evidence of dilution—in 13 equivalent to over 3 gallons of water per barrel. Of the 15,767 samples of beer examined for drawback, in only 7 was there over-declaration. Arsenic was found to be in slight excess of the limit in 27 of the samples of beer and brewing materials examined.

Cocoa and Chocolate.—Cocoa and its preparations are liable to cocoa duty on the amount of cocoa products in the goods; to sugar duty on sugar, glucose and allied sweetening materials; drawback is allowed on exported goods of home manufacture; duty on spirits and saccharin may be involved; non-Empire products, if they contain milk or coconut oil, are liable to Ottawa duties, and sometimes to a further 10 per cent. duty as confectionery. The total number of samples examined in connection with these duties was 14,508—an increase of about 2000, accounted for almost entirely by imported chocolates, the number of samples of which has now almost reached the 1930 level.

Coffee and Chicory.—Of the 52 import samples, 26 were dandelion root, and 4 of 1576 drawback samples were incorrectly declared.

Dangerous Drugs Act.—Of 24 samples, two were dilute opium extracts and one Indian hemp. The rest did not contravene the regulations.

Hydrocarbon Oils Duty.—The relevant Finance Acts stand as before, as also do the prescribed tests (see previous Report). The total number of samples examined was 14,957, of which 9406 were from imported, 5545 from exported, and 6 from wrecked goods. Seven samples of heavy oils were examined in connection with two prosecutions for using them for road transport without prior repayment of the 7d. per gallon rebate.

Hydrometers and Graduated Vessels.—A new instrument (the Tate Saccharometer) for use in breweries and distilleries has been approved by the Customs and Excise Department, and 100 have been calibrated and issued for use.

Import Duties Act and Ottawa Agreements Acts, 1932, account for 18,022 samples drawn from a wide range of products.

Spirits.—Of 3220 samples of gin and liqueurs on which drawback was claimed, the strength of spirits or the quantity of sugar was over-stated in 219 cases. Of exported spirituous preparations, 14,435 samples were examined; in 158 instances the spirit was over-claimed, and methyl alcohol was detected in 5.

Sugar, Glucose and Saccharin.—Of sugar itself, 23,800 samples were examined,

including 1864 from beet sugar factories, and of preparations containing sweetening matter, 52,359 samples were examined. Saccharin was searched for in 61 imported samples (many of which contained it); 526 samples of saccharin and articles containing it were examined to assess drawback on exportation, and 60 samples for assessment of duty for saccharin manufactured in this country.

Tea.—Of 12,153 samples of imported tea, 68, representing 219 packages, were reported against, 16 on account of the presence of foreign substances, and 52 as unfit for human consumption.

Tobacco.—Samples are primarily examined for detection and prevention of adulteration, for determination of appropriate rate of duty, and for control of denaturing processes. Of imported tobacco, 299 samples were examined for moisture-content. Four hundred and two (including 390 of cigarettes) samples of imported manufactured tobacco, of a total of 523, contained ingredients not allowed in this country. Of manufactured tobacco for home consumption, 6676 samples were taken for determination of moisture, and in 320 oil was determined. The number of samples involved in claims for drawback on exportation of manufactured tobacco, including cigars, cigarettes and snuff, was 109,305. In connection with "offal" tobacco, 55,688 samples were examined.

MINISTRY OF HEALTH.—Of the 120 samples of imported condensed milks, 13 were reported against—10 for offences connected with labelling, 3 of which were also below requirements in milk constituents, and 3 in which the quantity of whole milk, given as equivalent to the contents of the tin, was over-stated. One hundred and fifty nine samples were reported as contravening the Preservative Regulations, including 116 samples containing sulphur dioxide; and one sample of butter contained boric acid; 32 samples of soda-fountain preparations contained benzoic acid; egg-yolk and 8 samples of biscuits contained boric acid, and one sample of vegetables contained copper colouring matter.

FOOD AND DRUGS ACT.—Twenty samples of food and one drug were examined. The foods consisted of 14 milks alleged to be deficient in fat or non-fatty solids; two jams alleged to be deficient in fruit and one alleged to contain apple pulp; two sausages alleged to contain excess of sulphur dioxide, and one cheese alleged to contain formaldehyde; the drug was mercurial ointment alleged to be deficient in mercury. The results were in agreement with those put forward by the prosecution in all cases except one. In this case a sample of milk was examined for an alleged deficiency in fat, but later it was stated that the charge was a deficiency of non-fatty solids. By that time the milk had undergone further decomposition, and as it was not possible to make a satisfactory analysis, no certificate was issued.

D. G. H.

United Provinces and Central Provinces, Agra

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1936

THIS, the 72nd Annual Report, has been drawn up by Dr. S. N. Chakravarti, who has succeeded Mr. D. N. Chatterji as Chemical Examiner to the Government.

The total number of articles examined was 6504, as against 7066 in 1935.

HUMAN POISONING CASES.—A comparison of cases of human poisoning, in the three decennial periods 1901 to 1931, and from 1931 to 1935, shows that the average annual number of cases has increased from 292 to 410, and that the average percentage of detections has varied from 44·5 to 37·3. The low percentage of detection is partly due to the large number of trivial cases that are sent for chemical examination.

Another interesting point is that organic poisons are now being increasingly used, especially during the last five years, whereas 50 years ago preference was given to inorganic poisons. Probably one of the main reasons for this change is that with the spread of education, the criminal has gained the knowledge that the organic poisons give rise to less characteristic symptoms and are less easy of detection than the inorganic poisons.

The total number of cases of human poisoning investigated was 412, and poison was detected in 219. There was a surprising increase in the datura cases (28·1 per cent. of the detected cases). Arsenic was found in 21·8 per cent.; opium in 20·5; mercury salts in 5·4; aconite in 5·0; copper salts in 4·6; strychnine in 4·2; cyanides in 2·1 per cent. In 91 cases death was manifestly due to causes other than poisoning. Excluding such cases, the percentage of detection was 79·7.

ANIMAL POISONING.—There were 20 cases under this head, and poison was detected in 70 per cent. Arsenic was detected in 9 cases, kanher in 2, and aconite, madar juice and glass particles in one case each.

Department of Scientific and Industrial Research

Water Pollution Research

FINAL REPORT ON A SURVEY OF THE RIVER TEES*

IN this report a detailed description is given of the results of a chemical and biological investigation of the non-tidal reaches of the River Tees from its source on Cross Fell in the Pennines to Yarm. This investigation, which occupied a period of about four years, formed part of a comprehensive chemical, biological and hydrographical survey of the whole of the river and its tributaries from its source to the sea.

The object of the survey was to obtain data on the effects of the various discharges of sewage and trade effluents on the river and on the extent to which these polluting liquids should be purified before discharge, if serious pollution of the river water is to be avoided. In planning the work the aim was not merely to study the conditions affecting the River Tees, but also to provide basic information of value in considering problems of river pollution in general. The results of the hydrographical observations and of the chemical and biological survey of the Estuary were published some time ago as Water Pollution Research Technical Papers Nos. 2 and 5 (*cf.* ANALYST, 1936, **61**, 546). The three reports together give a complete description of the survey of the whole of the river. Into the estuary, mainly in the stretch of about seven miles from Stockton to Cargo Fleet, numerous industrial effluents and untreated sewage from a population of nearly 300,000 are discharged. As a result, large numbers of migratory fish attempting to pass through the estuary are killed each year, and the value of the salmon and sea trout fishery, which was formerly considerable, has greatly declined.

According to the report just issued, the non-tidal reaches of the River Tees can conveniently be considered as two parts—the first from the source at Cross Fell to the junction with the River Skerne at Croft Bridge, a distance of about 55 miles by river, and the second from Croft Bridge to Yarm, a distance of about 24 miles. These two parts are markedly different from one another.

* Technical Paper No. 6. Part III: The Non-Tidal Reaches—Chemical and Biological. Pp. xiii + 189, with map and 9 plates. H.M. Stationery Office, Adastral House, Kingsway, W.C.2, November, 1927. Price 12s 6d. net.

Above Croft the water is fairly soft, its hardness ranging from the equivalent of 5 to 10 parts of calcium carbonate per 100,000 parts; normally it is slightly alkaline in character, but at times of heavy flood it may be acid with peaty water from the moorlands near the source. From the source to Middleton-in-Teesdale, about 23 miles, the river is practically unpolluted, and chemical analysis showed little variation in composition. At all the positions examined in this region the same species of animals and plants were found, though their numbers varied from place to place, owing to differences in such physical conditions as current velocities and the nature of the river bed. Positions at which the current is swift and the river bed consists of large stones and boulders yielded smaller collections than the quieter stretches.

Between Middleton-in-Teesdale and Croft the effluents from several small sewage works are discharged into the river. At these positions definite chemical and biological evidence of pollution was obtained. For example, at points immediately below the sewage outfalls at Middleton-in-Teesdale, Cotherstone and Barnard Castle, chemical analysis revealed increased concentrations of substances associated with sewage and its products of decomposition, and the numbers of bacteria in the water also increased. As the quantity of sewage effluent at each of these three places is relatively small and the dilution by the river water is large, the effects observed were generally local, and the concentration of dissolved oxygen in the river water was not appreciably changed. The composition of the fauna and flora between Middleton-in-Teesdale and Croft showed no great variation from place to place, though the numbers of the various species tended to increase from the higher to the lower stretches.

At Croft the entry of the tributary river, the Skerne, causes a marked change in the chemical and biological characteristics of the Tees. The water of the Skerne is very hard, and it is heavily polluted with sewage effluent from the town of Darlington. As a result, the hardness of the water of the Tees at Croft is increased to between 10 and 20 parts per 100,000, and there is an increase in the quantity of organic matter in solution and in suspension. This organic matter undergoes decomposition and thereby reduces the concentration of dissolved oxygen in the water. The actual lowering of the concentration of dissolved oxygen varies with the rate of decomposition of the organic matter, and this in turn is dependent on temperature, increasing as the temperature rises. Although the river undergoes a certain amount of self-purification from Croft to Yarm, it does not regain the condition as observed above Croft.

The seasonal changes in the rate of self-purification of the river between Croft and Yarm were followed in detail, and the factors which affect the rate were studied by means of experiments in the laboratory. Of these factors, temperature and the amount of daylight are the most important. In the summer, oxidation of the polluting matter occurs rapidly, causing a marked reduction in the concentration of dissolved oxygen in the River Tees immediately below its confluence with the Skerne. The oxygen used in oxidising the organic matter is gradually replaced partly by oxygen evolved by plants growing in the water and partly by oxygen dissolved from the atmosphere. As a result, self-purification is almost complete in the warm summer months by the time the river reaches Yarm. In the cold winter months, however, self-purification proceeds much more slowly and is far from complete, even at Yarm.

Plants and animals are much more numerous in the Tees between Croft and Yarm than above Croft, owing to the presence of nutritive substances derived from the sewage effluent carried into the Tees by the Skerne. Some of the plants and animals occurred only in the heavily polluted part of the Skerne and in the polluted part of the Tees near Croft; these organisms are useful indicators of pollution.

The extent of the pollution in the non-tidal reaches of the River Tees does not seem to be detrimental to fish life, for brown trout are numerous and other fish,

such as grayling, dace, chub, gudgeon and roach, are found in various stretches of the river. The Skerne, however, is so badly polluted near Croft that its waters are frequently devoid of dissolved oxygen and fish life is impossible.

In this connection the general conclusion is drawn that in a river where there is a plentiful supply of oxygen, sewage in moderate quantity has no directly harmful effect on fish, unless it is in a septic condition and contains sulphide. When sewage is discharged, however, into a slow-flowing river, mud banks may be formed, which may provide the necessary anaerobic conditions for the production of sulphides. There is also a possibility that, although the fish are not directly affected, their food and spawning grounds may suffer.

Later sections in the Report deal with the macrophytic vegetation, the sessile microflora, the plankton, sewage fungus, the common species of algae, the animal life and the fauna list of the River Tees.

Atmospheric Pollution

THIRTY-SIX representatives of local authorities and other organisations co-operating with the Department of Scientific and Industrial Research met on November 30th at the offices of the Department in the half-yearly conference. The gathering included representatives from Barnsley, Birmingham, Cardiff, Dagenham, Glasgow, Halifax, Hull, Leicester, Liverpool, London, Royal Leamington Spa, Salford, Walsall, Willesden, Westminster, Wolverhampton, the British Commercial Gas Association, British Electrical Development Association, Cadbury Brothers and the Newcastle Gas Company.

Alderman Adams, J.P., M.P., of Newcastle, presided over the conference.

Dr. G. M. B. Dobson, F.R.S., Chairman of the Atmospheric Pollution Research Committee, presented the report on the progress of the investigations carried out under the Committee. He spoke, in particular, of the results which were being obtained in the special survey which was in progress in and around the City of Leicester, and he illustrated his statement with sketch maps, produced by the Survey, which showed how dust and sulphur gases had been observed to be distributed, over a limited period, during different wind conditions. He pointed out that, although the work of the Survey was not yet far advanced, it was already producing interesting results about a subject concerning which exact knowledge was much needed. There was every reason to hope that the ultimate results would be of great value.

The Conference also discussed two sources of atmospheric pollution which occurred in certain districts. On the motion of Bailie Munro (Glasgow), the representatives of local authorities unanimously agreed to request that a letter be addressed to the Ministry of Health protesting against the continuation of nuisance arising from burning colliery spoilbanks, and urging that action be taken to end it. On the motion of Dr. Burn (Birmingham), the representatives also agreed unanimously to ask the Department of Scientific and Industrial Research to consider and report on the possibility of research being undertaken to develop remedial measures to prevent nuisance caused by zinc-oxide fumes in certain stages of the manufacture of brass.

British Standards Institution

BRITISH STANDARD DENSITY-COMPOSITION TABLES FOR AQUEOUS SOLUTIONS OF SULPHURIC ACID, FOR USE IN CONJUNCTION WITH BRITISH STANDARD DENSITY HYDROMETERS

B.S.I. SPECIFICATION NO. 753—1937*

A British Standard Specification for Density Hydrometers (B.S.S. No. 718—1936; ANALYST, 1937, **62**, 129) has already been published, and the density-composition tables have been prepared primarily for use in conjunction with those hydrometers. Since, however, the composition of sulphuric acid solutions has been correlated directly with density, the tables may be used in conjunction with any method of determining density.

Appendices to the tables give details of the B.S. density hydrometers available for aqueous solutions of sulphuric acid, a note on the reading of B.S. density hydrometers in these solutions, examples of the use of the tables, and details of corrections to the readings.

APPARATUS AND METHODS FOR THE DETERMINATION OF THE PERCENTAGE OF FAT IN MILK AND MILK PRODUCTS BY THE BABCOCK METHOD

B.S.I. SPECIFICATION, NO. 755—PARTS I AND II—1937†

PART I. APPARATUS.—This work was begun by a Sub-Committee of the Dairy Research Committee of the Empire Marketing Board. When the Board came to an end on September 30th, 1933, arrangements were made for the British Standards Institution to continue the standardisation work. This Specification for apparatus has been based on a section of the report of the Empire Marketing Board's Sub-Committee and the comment received thereon.

It should be mentioned, however, that, whilst the specification has been prepared with a view to assisting in securing uniformity in the apparatus, it is not to be assumed that apparatus complying with the specification will necessarily meet the requirements of any official regulations of Government Departments of the British Commonwealth. Where apparatus is required to fulfil the requirements of such regulations reference should be made to the regulations themselves.

Part I of this Specification comprises the following sections:—Specification for (1) British Standard Babcock Bottle for Testing Milk—(2) British Standard Thirty per cent. 18 g. Babcock Bottle for Testing Cream—(3) British Standard Sixty per cent. 9 g. Babcock Bottle for Testing Cream—(4) British Standard Fifty per cent. 9 g. Babcock Bottle for Testing Cream—(5) British Standard Babcock Bottle for Testing Skim-Milk—(6) British Standard 17·6-ml. Milk Pipette for Babcock Test—(7) British Standard Graduated Cylinder for 17·6 ml. of Acid for Babcock Test—(8) British Standard Burette for Measuring Acid for Babcock Test—(9) Automatic Measure for Sulphuric Acid for Babcock Test—(10) British Standard 4-ml. Butyl Alcohol Pipette for Babcock Skim-Milk Test—(11) British Standard Funnel for Weighing Cheese for Babcock Test.

PART II. METHODS.—As was done in preparing the Specification for Apparatus (Part I), the British Standards Institution reviewed the report of the Sub-Committee of the Dairy Research Committee of the Empire Marketing Board in the light of the comments received, and based the British Standard Methods for the determination of the percentage of fat in milk and milk products on the section of the report dealing with these methods.

It is strongly recommended that in Great Britain apparatus, particularly Babcock test bottles, approved by the National Physical Laboratory as conforming with B.S.S. No. 755—Part I—1937, should be used, and that in other countries of the British Commonwealth either such apparatus, or apparatus tested at the recognised institutions in those countries, should be used.

Part II of the Specification comprises the following sections:—Specification for (1) Determination of the Percentage of Fat in Milk—(2) Determination of the Percentage of Fat in Skim-Milk, Separated Milk or Buttermilk—(3) Determination of the Percentage of Fat in Cream:—(*a*) Using 18 g. of cream and a standard thirty per cent. 18 g. Babcock bottle; (*b*) Using 9 g. of cream and a standard thirty per cent. 18 g. Babcock bottle; (*c*) Using 9 g. of cream and a standard sixty per cent. 9 g. Babcock bottle; (*d*) Using 9 g. of cream and a standard fifty per cent. 9 g. Babcock bottle—(4) Determination of the Percentage of Fat in Cheese.

* Copies of this Specification may be obtained from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net. Post free 3s. 9d.

† Copies of the two parts of this Specification may be obtained from the Publication Department, British Standards Institution, 28, Victoria Street, London, S.W.1. Price 3s. 6d. net each part.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Dialysis of Milk. L. H. Lampitt, J. H. Bushill and D. F. Filmer. (*Biochem. J.*, 1937, **31**, 1861–1873.)—The dialysable constituents of milk are affected to the same extent by acidification with a given quantity of lactic acid, whether this is added as a strong, or more dilute solution. The effect of the neutralisation of such acidity by caustic soda may be studied, for sodium and lactate ions in these concentrations have no effect on the dialysable constituents of milk. There is an approximately straight-line relationship between the concentration of dialysable calcium and of inorganic phosphorus of milk-powder solution and titratable acidity in the acidification stage, but if the added acid is neutralised, the original amounts of these constituents are not regained. This non-reversibility is not affected by the length of time (up to 9 days) that the milk is held at the high acidity. The amount of dialysable organic phosphorus is not affected by such treatment. If an acidified, raw, separated milk is neutralised, an almost complete recovery of the original amounts of dialysable calcium, magnesium and inorganic phosphorus is obtained, although the calcium figure remains slightly above the normal. Shaking for 14 days has been found to reduce the amounts of dialysable magnesium and calcium and to increase the amount of dialysable inorganic phosphorus in raw separated milk, but to have no effect on these constituents in milk-powder solution. When this treatment was applied to neutralised, acidified milk-powder solution or to similarly treated raw, separated milk, these constituents were diminished. By means of such shaking an approximate reversibility of the dialysable inorganic constituents of milk-powder solution after acidification and neutralisation may be obtained. For raw separated milk, shaking is not entirely necessary, and a prolonged treatment caused difficulties with the control of acidity and with the apparent phosphatase action on the dialysable organic phosphorus. It is suggested that the salt equilibrium of milk is normally unstable, and that this equilibrium may be shifted by agitation of the milk. The treatment of the milk in the preparation of milk-powder appears to stabilise the salt equilibrium. It is not possible to compare milks of differing acidity by adjusting the milks before dialysis to a standard acidity, since the reactions caused by acid (*e.g.* incipient souring) are not strictly reversible. The amounts of the dialysable constituents have been determined by the "static" method under controlled conditions. The following figures have been obtained on raw, pasteurised and dried, separated, "average" milks.

	Total, per cent.	Dialysable (as per cent. of the total present)
Inorganic phosphorus ..	0·63–0·77	33–43
Organic phosphorus ..	0·31–0·38	7–15
Calcium	1·27–1·44	25–42
Magnesium	0·10–0·15	62–83

S. G. S.

Fluorescence of Egg-shells and Micro-determination of Phosphoric Acid in the White of the Egg. J. Straub, G. A. Van Stijgeren, and W. J. Kabos. (*Chem. Weekblad,* 1937, **34**, 732–733.)—The fluorescence of egg-shells is due principally to porphyrin, and is normally red in colour. There is evidence, however, that the fluorescence changes on ageing, and this has been suggested as a means of assessing the age of eggs. Of the 50 eggs (guaranteed to be one day old) examined by the authors, 27 had a purple-red fluorescence, 16 were red, 5 blue and 2 colourless; 43 could have been described as "red," the other 7 being definitely blue or colourless. The samples were stored in the dark, and examined at intervals of 1 week. In general, the purple-red colour was retained for 2 weeks, the red colour for 8 weeks, and the blue colour for 1 week, the colourless shells remaining unchanged. In every instance the change was in the direction red—blue—colourless, but it is considered that the rate of change is an individual characteristic of each egg, and that it does not afford a reliable criterion of age. Inorganic phosphates in egg-white may be determined by the method of B. H. Molanus (*Diss. Utrecht,* 1935; see also Radeff, *Z. Fleisch- u. Milchhyg.,* 1935, **45**, 363; and Janke and Jirak, *Biochem. Z.,* 1934, **271**, 309). To 2 ml. of sample and 8 ml. of water are added 5 ml. of a solution containing 20 g. of hydroquinone in a mixture of 1 litre of water and 1 ml. of sulphuric acid, and 5 ml. of a solution of 25 g. of ammonium molybdate in 500 ml. of N sulphuric acid. After 15 minutes 20 ml. of a solution containing 20 g. of anhydrous sodium carbonate and 37·5 g. of sodium sulphite in 1200 g. of water are added, and the blue colour is allowed to develop for 3 hours, after which the solution may be filtered and the colour assessed by means of the scale compiled by Molanus. The authors found that most of the 50 eggs examined, whether 1 or 9 weeks old, fell below the lowest limit of the Molanus scale. In six instances the P_2O_5-content of 2 ml. of sample was 13γ (equivalent to a Molanus value of 1), the maximum figure found being 31γ (Molanus value 9). It is concluded that, although there is a general tendency for the phosphate-content of the egg-white to increase with the age of the egg, it is not a reliable criterion of the age.

J. G.

Colorimetric Determination of Lactic Acid in Fruit and Fruit Products. F. Hillig. (*J. Assoc. Off. Agr. Chem.,* 1937, **20**, 605–610.)—The colorimetric method for the determination of lactic acid in milk and milk products (Hillig, *J. Assoc. Off. Agr. Chem.,* 1937, **20**, 130; Abst., ANALYST, 1937, **62**, 614) can be applied to fruit and fruit products. Jam or jelly (50 g.) is boiled with about 150 ml. of water for 15 minutes, cooled, made up to 250 ml. and filtered through cotton-wool. Fifty ml. of the filtrate are acidified with 1 ml. of dilute sulphuric acid (1 + 1) and extracted with ether in the continuous extractor for 3 hours (*loc. cit.*). With fruit juices, 10 ml. of the material are placed in the extractor with 40 ml. of water and, after acidification with 1 ml. of the dilute acid, are extracted for 3 hours. Subsequent treatment of the extract is as described for milk and milk products (*loc. cit.*) but, in making the photometric comparison, a filter transmitting near 460$m\mu$ may be used instead of one transmitting near 450$m\mu$. If A is the volume of the aliquot portion taken for the final determination,

the amount of the sample it contains is $\frac{50}{250} \times \frac{50}{110} \times \frac{100}{55} \times A$, or 0·1653 A. The accuracy of the method was tested by determining the amounts of lactic acid in samples of commercial grape juice and authentic grape jelly to which known amounts of lithium lactate had been added. The method was found to be satisfactorily accurate and was then applied to the determination of the lactic acid content of a number of authentic fruits. The following are some of the results obtained in mg. of lactic acid per 100 gm.:—Apple (Stayman) 9·1, 8·8; apple (Winesap) 5·6, 5·3; apricot (Royal) 8·7, 9·4; blackberry (Mammoth) 20·2, 19·3; blackberry (Himalaya) 15·0, 14·3; currant (red) 6·1, 6·1; grape (Concord) 13·4, 13·4; peach (Elberta) 13·2, 13·2; pineapple (Hawaiian, 2 samples) 10·5, 11·3 and 14·8, 14·8; plum (Burbank) 17·2, 16·1; plum (damson) 32·1, 33·7; raspberry (red) 12·8, 12·8; strawberry (Banner) 15·2, 15·0. The following results are expressed in mg. of lactic acid per 100 ml. of the juice:—Grape fruit 9·7, 9·5; lemon 7·9, 7·9; orange (Valencia Florida) 6·2, 6·2; orange (seedless California) 3·5, 3·2; tomato (average of 13 samples) 5·7. The following are a selection of the results found with commercial fruit products:—Blackberry jam 94·1, 91·5; blackberry jelly 284·4, 283·5; currant jelly (2 samples) 259·6, 261·7 and 8·0, 8·8; grape jelly (2 samples) 7·9, 7·6 and 298·3, 292·0; liquid pectin (not acidified) 37·0, 36·6; liquid pectin (acidified) 3391·0, 3351·0; dry pectin 45·4, 44·2; raspberry jam (3 samples) 77·8, 77·0 and 17·5, 16·7 and 6·1, 6·1; strawberry preserves (3 samples) 275·3, 271·7 and 70·6, 70·0 and 32·2, 32·2. Samples which did not conform to the American statutory standards for fruit-content invariably showed a high lactic acid content, indicating the presence of lactic acid either derived from commercial pectin or added as an acidulant. The method may be applied to the determination of lactic acid in wine, of which it is a normal constituent. Owing to the tendency of some wines to froth in the extractor, a preliminary precipitation of the substances causing frothing is necessary. The wine (50 ml.) is mixed with 100 ml. of alcohol, shaken vigorously, diluted to 250 ml. with alcohol, and filtered through paper. A portion (200 ml.) of the filtrate is evaporated to about 25 ml., diluted with 50 ml. of water and again evaporated to 25 ml. It is then diluted to 200 ml. with water, and 50 ml. are acidified with dilute sulphuric acid and placed in the extractor, the subsequent procedure being as for milk and milk products (*loc. cit.*). The amount of lactic acid found in wines varied from 106·8 (Riesling, New York) to 485·5 (Zinfandel, California) mg. per 100 ml. A. O. J.

Estimation of Worm and Insect Fragments in Tomato Products. C. D. Wilder and M. A. Joslyn. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 648–655.)—The method used at present is essentially that described by Howard (*Food Industries*, 1935, **7**, 321) and Harrison (*Canner*, 1937, **34**, 9, 18). The tomato product (200 ml.) is mixed with a small volume of petrol and then diluted with water. The petrol separates the insect and worm fragments from most of the pulp, and carries them to the surface. The petrol layer, with a few ml. of the underlying aqueous layer, is filtered through a small filter-paper, and the number of insect and worm fragments is determined by examination under a low-power binocular microscope having a large field. A study of this method showed that,

with the exception of a few small setae which float on the surface, the insect and worm fragments settle finally at the petrol-water interface, and that the separation of the fragments from the pulp is seldom complete. By examination of the conditions under which the particles settle, and of the effect of a number of oxidising agents upon the residual pulp associated with them, it was found that the following modification of the method results in the destruction of the natural colouring matter and the removal of the emulsifying agents, thereby yielding a sediment containing less pulp and gummy matter than that obtained by the original method. A quantity of the tomato product (200 ml. of sauce, juice or catsup, or 100 ml. of paste) is placed in a litre separator, 35 ml. of petrol are added, and the mixture is shaken until thoroughly emulsified. The emulsion is then acidified with 200 ml. of 12 *N* sulphuric acid and 150 ml. of an aqueous 10 per cent. solution of potassium permanganate are added cautiously, 50 ml. at a time, to prevent excessive foaming. After each addition the separator is shaken with a rotatory motion until all traces of the permanganate and manganese dioxide have disappeared and, after the last addition, it is filled with water and allowed to stand for 1 minute. The lower layer of water and pulp is drained off to within 2 in. of the tap, 200 ml. of water are added and drained off as before, and washing is continued with successive 100-ml. portions of water until the aqueous layer is free from pulp. Finally, the aqueous layer is drained off to within half-an-inch of the tap, and the remaining water and petrol mixture is filtered through a 7-cm. filter-paper, the separator being washed out with water. The paper is then examined under the microscope. This modification reduces the time required for the preparation of the sample from about 30 minutes to about 10 minutes and, owing to the cleaner state of the sediment, the time required for microscopical examination is also reduced. A. O. J.

Rapid Determination of Iron in Pharmaceutical Preparations by means of Cupferron and an Immiscible Solvent. S. M. Berman, J. J. Chap and D. M. Taylor. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 635–638.)—The observation of Baudisch and King (*J. Ind. Eng. Chem.*, 1911, **3**, 629)—that the precipitate formed with iron salts by cupferron is soluble in various organic solvents—suggested the following method for the determination of iron, which was found to be generally applicable to pharmaceutical preparations containing iron. To the solution, containing not more than 100 mg. of iron, sufficient hydrochloric acid is added to make the total acidity equivalent to at least 10 ml. of 4 *N* acid. An aqueous, 6 per cent. solution of cupferron is then added until a white precipitate is momentarily formed. Chloroform (10 ml.) is added, and the mixture is shaken vigorously for 15 seconds, or gently for a longer period. When the layers have separated, more reagent is added until the white precipitate re-appears. (In the presence of iron, the white precipitate rapidly changes to pinkish-brown.) This procedure is repeated without removing the chloroform until, after alternate treatment with the reagent and shaking out, the aqueous layer is free from any turbidity but that due to suspended chloroform. The chloroform layer is drawn off into a second separator, and the aqueous layer is washed with small amounts of chloroform until this solvent remains colourless. The combined chloroform extfacts are

washed with 10 ml. of water and transferred to a weighed dish suitable for ignition. The solvent is evaporated on the steam-bath, and the residue is heated at 150° to 300° C. until fuming ceases, and finally at 500° to 700° C. until its weight is constant. The residue of ferric oxide may, if preferred, be determined volumetrically by the method of Zimmerman–Reinhardt, as described by Jones and Jeffery (ANALYST, 1909, **34**, 306). The method was applied to the determination of iron in solutions of ferrous and ferric salts containing no organic matter and solutions containing, in addition, different amounts of various substances commonly occurring in pharmaceutical preparations, *e.g.* citrates, acetates, glycerol, iodine, sucrose, strychnine, hypophosphites, glycerophosphates, quinine and manganese. The results were in satisfactory agreement with those obtained by removing the organic matter by ignition before determining the iron. When used to determine the amount of iron in syrup of ferrous iodide and in green iron and ammonium citrate, this method gave results agreeing with those obtained by the official methods of the U.S.P. XI. A. O. J.

Ergocristin and Ergocristinin, a New Pair of Alkaloids from Ergot. A Stoll and E. Burckhardt. (*Z. physiol. Chem.*, 1937, **250**, 1–6.)—A new pair of alkaloids, named ergocristin and ergocristinin, has been isolated from ergot. These have the same empirical formula as ergotoxin and ergotinin, namely, $C_{35}H_{39}O_5N_5$. Ergocristin melts at 155°–157° C. with decomposition, gives $[\alpha]_D$ in chloroform − 183°, and has a high physiological activity. Ergocristinin melts, with decomposition, at 214° C., gives $[\alpha]_D$ in chloroform + 366°, and has a lower physiological activity (*cf.* Barger, ANALYST, 1937, **62**, 340). S. G. S.

Analysis of Aminophylline. F. Reimers. (*J. Assoc. Off. Agr. Chem.*, 1937, **20**, 631–635.)—Aminophylline contains theophylline, ethylenediamine and water. In a critical examination of the methods used for the determination of theophylline in theophylline–sodium acetate, Reimers (*Dansk. Tids. Farm.*, 1935, **9**, 11) found that the argentometric method gives high results, the iodimetric method low results approaching more nearly to accuracy when a large excess of iodine is used, and the methylation method of Self and Rankin (*Quart. J. Pharm. Pharmacol.*, 1931, **4**, 346) correct results. The last method may be simplified and the methylation to caffeine omitted by using for extraction a mixture of 1 volume of isopropyl alcohol and 3 vols. of chloroform. Aminophylline (0·3 g.) is dissolved in 2 ml. of water, and the solution is slightly acidified to methyl red with dilute hydrochloric acid. The liquid is shaken for 1 minute with 25 ml. of the chloroform and isopropyl alcohol mixture, and the extract is filtered into a weighed flask. Extraction is repeated with 20-, 20- and 10-ml. portions of the solvent, the combined extracts are evaporated, and the residue dried at 100° C. to constant weight. To obtain the weight of crystalline theophylline, the weight of anhydrous theophylline is multiplied by 1·100. The method is applicable to solutions containing excess of acid and to slightly alkaline solutions, if the number of extractions is increased to six or seven, and to the isolation of theophylline from tablets or soluble compounds, such as theophylline–sodium acetate. With the last substance it is necessary to remove the acetic acid by three evaporations with dilute sulphuric acid. Electrometric titration of ethylenediamine shows that this substance can

be titrated as a bivalent base to *p*H 4·6. The best indicator is bromocresol green, the end-point of the titration being the appearance of the green colour. The result is not influenced by the presence of theophylline. Since aminophylline loses ethylenediamine when exposed to air at the ordinary temperature and when dried over calcium chloride, these methods cannot be used for the determination of its water-content. When it is dried at 125° C., the water and ethylenediamine are completely removed in a few hours and, by deducting the ethylenediamine-content from the loss in weight, the water-content can be ascertained. At 105° C. drying proceeds more slowly and must be continued for 24 hours. The residue left after drying aminophylline at 125° C. should consist of pure theophylline, and, when combined with an examination of the purity of the residue, this affords a rapid and simple method of determining the theophylline-content. A. O. J.

Biochemical

Volumetric Method for the Determination of Potassium in Biological Materials. H. E. Harrison and D. C. Darrow. (*J. Biol. Chem.*, 1937, **121**, 631–635.)—The material is ashed, and a suitable amount of the ash is dissolved in water or dilute hydrochloric acid. Sufficient chloroplatinic acid (26·5 g. of chloroplatinic acid, $H_2PtCl_6.6H_2O$, dissolved in 100 ml. of *N* hydrochloric acid) is added to combine with all the potassium and sodium. The solution is then evaporated until the salts separate, but still look moist on cooling. To the residue a small amount of 80 per cent. acid alcohol is added, and the solution is filtered, preferably by means of automatic transfer by suction, as recommended by Pregl (*Quantitative Organic Microanalysis*, translated by E. Fyleman, Philadelphia, 2nd Ed., 1930, 133). The residue is washed in the usual way until the filtrate is free from chloride. The separated potassium platinic chloride is dissolved in a small amount of hot water, and made up to a definite volume. To a suitable portion of this solution 0·4 to 0·5 ml. of a 15 per cent. solution of sodium bisulphite is added, and the whole is boiled for one minute. Three ml. of 0·05 *N* silver nitrate solution are added, followed by 2 to 4 drops of 30 per cent. hydrogen peroxide solution. The solution is boiled, cooled in ice-water and titrated by the usual Volhard technique. The titration of the chloride should be carried out on 0·004 to 0·04 mg.-mol. of potassium, and the end-point of the titration is best when the volume of the solution does not exceed 10 ml. The results are calculated from the formula: mg.-mol. of K $= (7{\cdot}54 - x)\ 0{\cdot}02/3$ where $x =$ ml. of 0·02 *N* ammonium thiocyanate solution used. The acid 80 per cent. alcohol is prepared by adding a small quantity of potassium platinichloride to 15 ml. of approximately *N* solution of nitric acid; after shaking, 80 ml. of 95 per cent. ethyl alcohol are added, and the mixture is filtered before use. The results obtained were accurate to within 1 per cent. of the theoretical. S. G. S.

Staining the Acrospires of Malt. C. A. Kloss. (*J. Inst. Brewing*, 1937, **43**, 471.)—If malt-corns are boiled for a few minutes in an approximately 2 per cent. solution of copper sulphate and then allowed to soak (presumably in it) for about 1 hour, a constituent of the acrospire assumes a distinct bluish colour, which facilitates considerably the judgment of relative lengths and, therefore, of malt

"growth." Examination of a cross-section of the acrospire shows that the colour persists through it. Green malt at various stages of growth is not stained, but even under-modified malts show the blue colour after kilning. J. G.

Milk-Clotting Action of Papain. A. K. Balls and S. R. Hoover. (*J. Biol. Chem.*, 1937, **121**, 737–745.)—The milk-clotting component of papain agrees closely with the current conception of a papain proteinase. It is activated by hydrogen sulphide, cysteine, and cyanide, has a high temperature-optimum and is not inhibited, but rather is activated, by phenylhydrazine. A study of the kinetics of the clotting effect showed that the time required is a straight-line function of the enzyme concentration, as with chymotrypsin, but with the difference that a quantity of the enzyme—constant for any given preparation—is inhibited by the milk. The relationship is accurately expressed by an equation of the form $(E—C)t = K_1$, where E is the weight of enzyme in mg., C is the amount of the enzyme inhibited and t is the time in minutes. E—C is therefore the available enzyme. For the test, 20 g. of dried milk are ground to a smooth paste with a small amount of diluted acetate buffer, *p*H 4·60, and diluted with the buffer to 100 ml. The liquid is filtered through cheese-cloth and is stable for several weeks if kept in an ice-chest. Various dilutions of the enzyme in water are used, and the time is noted for a given dilution to clot 10 ml. of the milk at 40° C. The rapidity and simplicity of the technique, and the probable connection between the clotting time and the proteolytic properties of papain, make the determination of the clotting power an aid in describing the activity of this mixture of enzymes. S. G. S.

Pectic Enzymes. I. The Determination of Pectin-Methoxylase Activity. Z. I. Kertesz. (*J. Biol. Chem.*, 1937, **121**, 589–598.)—The proposed method is essentially the same as that already used for lipases and consists in demethoxylation, whereby the carboxyl groups of the galacturonic acids in pectin are freed and rendered titratable. The reaction mixtures contain 30 ml. of an approximately 1 per cent. solution of citrus pectin, and 10 ml. of enzyme (pectin-methoxylase—"pectase" of Frémy), alkali and water. The enzyme solution is added to the pectin solution in a 100-ml. Erlenmeyer flask, 5 drops of methyl red solution are added, and the *p*H is adjusted with 0·1 *N* caustic soda solution to the point where the last pinkness of the mixture has been discharged by 1 drop of alkali (*p*H 6·2). A 5-ml. micro-burette, with 0·02 ml. divisions, should be employed. The volume of the reaction mixture is adjusted to 40 ml. with distilled water. Before the mixing, all components are warmed to 30° C., and this temperature is maintained during the reaction. Titration is carried out every 10 minutes. The number of mg. of methoxyl split off during 30 minutes (total ml. of 0·1 *N* alkali × 3·1), divided by the number of ml. of enzyme solution used, gives the mg. of methoxyl split off by 1 ml. of the enzyme solution, and this is termed the "pectin-methoxylase units" per ml. of solution. This figure, divided by the weight of dry material contained in 1 ml. of enzyme solution, gives the number of mg. of methoxyl split off by 1 g. of material or the "pectin-methoxylase units" per g. of dry material. Tomato-juice, leaves of the lilac plant (*Syringa vulgaris*), cherry juice, alfalfa juice and juice from hot-house grown tobacco plants were used as sources of the enzyme. S. G. S.

Water-soluble B-vitamins in Yeast, Flour and Bread. A. M. Copping and M. H. Roscoe. (*Biochem. J.*, 1937, **31**, 1879–1901.)—Various yeasts, flours and bread made from them have been examined for the separate members of the vitamin B complex, by means of the rat-growth methods for the estimation. The international standard acid clay adsorbate was used as the standard for vitamin B_1, and a bakers' yeast (sample III) was taken as the standard for vitamin B_2. Brewers' yeast was richer in vitamin B_1 than bakers' yeasts, except in one specially fortified sample. All the yeasts examined were equally good sources of the vitamin B_2 factors other than flavin, and the variation of this component was not large, but it was the limiting factor for growth in two samples of bakers' yeast. The factors other than flavin were the limiting factors in the brewers' yeast and in one bakers' yeast. Straight-run unbleached and bleached white flours were equal and fairly good sources of vitamin B_1, and no loss of activity was found after storage for 12 months. These flours were representative of the ordinary flours commercially used in this country for making bread. A sample of patent flour was found to contain no appreciable amounts of vitamin B_1, but wholemeal flour was about three times as rich in this vitamin as the straight-run white flours. Straight-run white flour and wholemeal flour did not differ greatly in their contents of flavin or of vitamin B_2 factors other than flavin; the wholemeal contained rather more of each constituent. The flours were all limited in their growth-promoting activity by their flavin-contents, which were decreased by bleaching and keeping, while the other B-vitamins were not affected. The vitamin B_1 contents of white bread made by the short- or long-dough processes were equal and about one-third as great as that of wholemeal bread. The white bread made with baking powder contained no demonstrable vitamin B_1. Wholemeal bread was a better source of vitamin B_2 complex and its constituents than white bread, but the difference was not so marked as that for vitamin B_1. Flavin was in every instance the limiting factor for growth when the bread was fed as a source of vitamin B_2 complex. When the dry weight was considered, the bread contained substantially the same amount of the B-vitamins as the flour from which it was made, excepting only the baking powder bread, for which the content was less than that of the flour. The small amounts of yeast used did not materially affect the vitamin-content of the bread, and no evidence was obtained of synthesis or destruction of vitamins during the baking process. Owing to the large amount of bread consumed, the vitamin B content, although lower than that of many other foods, becomes a significant amount in the human diet. S. G. S.

Fermentation Test for Vitamin B. II. A. S. Schultz, L. Atkin and C. N. Frey. (*J. Amer. Chem. Soc.*, 1937, **59**, 2457–2460.)—Crystalline vitamin B_1 and the synthetic product are powerful accelerators of the alcoholic fermentation of sugars by yeast. Hence, a rapid method of vitamin assay has been devised, which is based on the volume of carbon dioxide liberated in 3 hours by the fermentation of dextrose in the presence of various known amounts of vitamin B_1 (*cf. J. Amer. Chem. Soc.*, 1937, **59**, 948–949; Abst., ANALYST, 1937, **62**, 567). The test is not specific for "thiamine" (*i.e.* for vitamin B_1); the reaction is also given by 2-methyl-5-ethoxymethyl-6-aminopyrimidine, which is used in the synthesis of thiamine

The aminopyrimidine compound, which has been found only in autoclaved yeast, does not stimulate rat-growth, and its presence may be suspected if any significant difference occurs between the gas and rat tests for a particular type of product. Results of the gas test must be correlated from time to time with those of animal-growth. When a series of vitamin concentrates or yeasts is analysed, the accuracy with which results can be checked is as great as the accuracy of the gas measurement. The quantity used is equivalent to 2 to 5γ of pure thiamine. For 4γ and 2γ respectively, if the tests are repeated over any period of days, there is an unsatisfactory variation in the total gas-production (*i.e.* control plus stimulation). The daily difference, $\Delta_{4\gamma-2\gamma}$, however, is constant (see Table). In the following table the standard deviation, $\sigma\Delta_{4\gamma-2\gamma}$, is expressed in terms of International B_1 units ($4{\cdot}0\gamma$ of pure thiamine being equivalent to one International unit).

AVERAGE OF 14 PAIRS OF MEASUREMENTS

	Average ml. of gas	A.D. ml. of gas	σ Gas ml.	σ Int. B_1 units
4γ ..	329·2	8·76	9·95	—
2γ ..	264·7	6·34	8·07	—
$\Delta 4\gamma$–2γ	64·5	3.3	4·23	0·032

In the fermentation of sugars, the "yield" of gas is increased by the presence of thiamine or of the pyrimidine compound used in its synthesis. Details of experimental work are given. E. B. D.

Chemical Identification of Ascorbic Acid in Urine. P. J. Drumm, H. Scarborough and C. P. Stewart. (*Biochem. J.*, 1937, **31**, 1874–1878.)—By the use of 2:4-dinitrophenylhydrazine the ascorbic acid from 12 litres of urine was obtained in the form of 20 mg. of the hydrazone of dehydroascorbic acid, purified by repeated adsorption on aluminium oxide and crystallisation from acetic acid and from acetone or from acetone-alcohol. The substance was identified by its crystalline form, its m.p., mixed m.p., colour reactions with sulphuric acid and with sodium hydroxide, absorption in the visible spectrum, and distribution between two immiscible solvents. A second hydrazone has been isolated, but not yet identified. S. G. S.

Vitamin E (Tocopherol). J. C. Drummond and A. A. Hoover. (*Biochem. J.*, 1937, **31**, 1852–1860.)—In the fractionation of the unsaponifiable matter from wheat-germ oil, it has been found that extraction of the petroleum spirit solution with absolute or 92 per cent. methyl alcohol does not give such a satisfactory separation as does the chromatograph method using aluminium oxide. Various stages in an attempt to isolate pure vitamin E are described, and the purest specimen obtained by the authors is compared with that obtained by Emerson in America. The purest fraction obtained by them was β-tocopherol, showing $E^{1\%}_{1\,cm.}$ $296m\mu$ = 79 with a high persistence and an iodine value of 149. Examination of the spreading properties indicated that one cross-section of the vitamin must be at least 8 sq. $m\mu$ and the other less than 6 sq. $m\mu$, and that the vitamin has probably a sterol-like structure with a long side-chain. S. G. S.

Toxicological and Forensic

Convallatoxin. L. F. Fieser and R. P. Jacobsen. (*J. Amer. Chem. Soc.*, 1937, **59**, 2335–2339.)—The structural formula for convallatoxin, tentatively suggested by Tschesche and Haupt (*Ber.*, 1936, **69**, 459) is considered inadmissible. Tschesche and the authors have now found derivatives prepared from convallatoxin, after elimination of the sugar residue, to be identical with the corresponding derivatives of strophanthidin (*i.e.* with mono-, di- and tri-strophanthidin). These results, together with earlier work by Tschesche, prove the (un-isolated) aglycone, convallatoxigenin, to be identical with strophanthidin. The sugar component of convallatoxin is a methyl pentose which is very probably identical with *l*-rhamnose (*cf.* Tschesche and Haupt, *loc cit.*). The experimental work is described.

E. B. D.

Destruction of Organic Matter with Perchloric Acid. E. Kahane. (*Z. anal. Chem.*, 1937, **111**, 14–17.) (*Cf.* ANALYST, 1937, **62**, 226.)—The author has employed perchloric acid for a number of years in biological and toxicological work for the destruction of organic matter, in quantities up to several thousand grams. In his published methods he employs either nitric and perchloric, or nitric, sulphuric, and perchloric, acids. With either mixture a thorough preliminary attack with nitric acid is made. Perchloric acid begins to act at 160° C., a temperature at which the nitric acid has been expelled. The mixture of perchloric acid and organic matter may explode unless a sudden rise in temperature is prevented; this is achieved by the presence of an excess of perchloric acid, which acts as a diluent; sulphuric acid acts in like manner. The latter is used for substances not readily attacked by nitric acid alone (fatty acids, paraffins). It is, however, dangerous to apply perchloric acid to bodies with which it is immiscible, as the reaction is then confined to the zone of contact and local over-heating cannot be controlled. When sulphuric acid is used, the reaction mass is kept at 160° to 180° C., and perchloric acid, or a mixture of nitric and perchloric acids, is added in small amounts.

W. R. S.

Lead in Urine and Faeces. R. H. K. N. Bagchi and H. D. Ganguly. (*Ind. J. Med. Research*, 1937, **25**, 147–154.)—Fifty-three normal cases were examined to find the normal limit for lead in the urine and faeces of Indians. The method used for the determination was that of Lynch, Slater and Osler (ANALYST, 1934, **59**, 787), modified according to a suggestion put forward by Lynch *et al.*, but not confirmed by them. The samples of urine were collected for 24 hours, without addition of preservative, in a large Pyrex flask specially cleaned for this purpose; the faeces were collected from fresh morning specimens and were kept covered in a large Pyrex Petri dish. Fresh faeces were used for the determinations; the lead-content of fresh faeces should be multiplied by 4·52 to give the value for dry faeces (dried to constant weight). Five hundred ml. of urine or 25 g. of faeces were oxidised with nitric and sulphuric acids, and the lead was extracted with a chloroform solution of diphenylthiocarbazone (dithizone); the extract was oxidised in the same way and treated with ammonia, ammonium acetate, sodium cyanide, and sodium sulphide, and a colorimetric determination

was made in the usual way. The modification introduced consisted in treating the oxidation products, before and after extraction with dithizone, with saturated ammonium oxalate solution, followed by destruction of the oxalate with sulphuric acid. This modification inhibits the development of the very deep yellow colour which is useless for matching. Blank tests with known weights of all the reagents and with the same glassware as was used in the experiments were carried out, and the results were deducted from the figures obtained in the actual determinations. Tables reproduce the results for all the individuals examined. The results are summarised in Table I.

TABLE I

Lead in normal urine and faeces (mg. per litre or kg.)

	Urine			Faeces (fresh)		
	Minimum	Maximum	Average	Minimum	Maximum	Average
Hindus ..	nil	0·016	0·008	0·08	0·14	0·11
Mohammedans	nil	0·026	0·014	0·10	0·16	0·13
Anglo-Indians	0·024	0·040	0·031	0·13	0·18	0·15

Diet is probably the determining factor for the differences in the quantities of lead excreted by Hindus, Mohammedans and Europeans. The total quantity of lead eliminated by Indians in the faeces is about 10 times the amount in urine; for Anglo-Indians it is about 5 times. Nineteen printing-press employees and others, some suspected to be, and others known to be suffering from lead-poisoning, were also examined to ascertain the quantities of lead excreted by them. The results are summarised in Table II.

TABLE II

Lead in urine and faeces of printing press employees (mg. per litre or kg.)

	Minimum	Maximum	Average
Urine	0·004	0·53	0·107
Faeces	0·100	4·50	1·530

Examination of both urine and faeces is useful for the chemical diagnosis of lead poisoning.

E. M. P.

Agricultural

Determination of Manganese in Plants. N. D. Costeanu. (*Bull. Soc. Chim.*, 1937, **4**, 1800–1803.)—The method is based on the formation of characteristic coloured stains of various intensities which are obtained by the action of solutions of potassium permanganate of known concentrations on filter-papers impregnated with solutions of appropriate reagents (*e.g.* acidified hydrogen peroxide, alkaline potassium ferricyanide, ammonium sulphide, alkaline arsenious oxide and manganous sulphate). The test-papers are prepared by simple immersion, care being taken to avoid air-bubbles, and are finally dried in warm air in the vessel in which impregnation has taken place. The sample to be tested is ashed according to Bertrand's method (*id.*, 1911, **4**, 362), any manganese present being converted

into permanganate by the potassium persulphate and silver nitrate method. The solution is then diluted to a suitable volume, and 1 drop of this is allowed to fall on the reagent-paper, the resulting stain being compared with a set of standard stains prepared in the same way from a range of 8 solutions of potassium permanganate containing 0·001 to 1 mg. of manganese per ml. Manganous sulphate is the most sensitive reagent and produces permanent dull yellow stains, even when the drop tested contains only 0·000001 mg. of manganese. With arsenious oxide the sensitiveness is 0·00001 mg. of manganese, and the colours of the stains change from red at first, to greenish-yellow and then to dull yellow. The two sets of stains mentioned above are reproduced photographically in the original paper; the other reagents are less sensitive. J. G.

Furfuraldehyde Yield of Soil. C. N. Acharya. (*Biochem. J.*, 1937, **31**, 1800–1804.)—The bromine titration method of Powell and Whittaker (*J. Soc. Chem. Ind.*, 1924, **43**, 35T) has been compared with the usual gravimetric phloroglucinol method for the estimation of total furfuraldehyde yield of soils and plant materials admixed with soil. In the absence of soil the two methods gave concordant results, but in the presence of soil both methods gave low results owing to the presence of oxidising substances (such as ferric and manganese compounds and nitrate) in the soil, which cause oxidation of a portion of the furfural during the distillation with 12 per cent. hydrochloric acid. The addition of stannous chloride solution (about 1 ml. of 10 per cent. solution per g. of soil) serves to reduce these oxidising agents and to enable a satisfactory recovery of furfuraldehyde to be obtained. Excess of stannous chloride, however, tends to produce methyl furfuraldehyde, which reacts with bromine and increases the "apparent" furfuraldehyde yield, as determined by bromine titration. This interference is much less when the phloroglucinol precipitation method is used, as methyl furfuraldehyde is only partly precipitated by this reagent, and even this interference can be prevented by treating the precipitate with boiling alcohol, in which the impurity is easily soluble. It is concluded, therefore, that for soils and plant materials mixed with soil, distillation of the material with 12 per cent. hydrochloric acid solution in the presence of stannous chloride, and precipitation of the furfuraldehyde with phloroglucinol, followed by extraction of the precipitate with boiling alcohol, is preferable to the bromine titration of Powell and Whittaker. S. G. S.

Organic

Determination of Primary Alcohols and Certain Secondary Alcohols by means of Phthalisation and Identification of Esterifiable Alcohols in the Form of Acid Phthalates. S. Sabetay and Y. R. Naves. (*Ann. Chim. anal.*, 1937, **19**, 285–289.)—A quantity of the sample (*e.g.* essential oil) equivalent to 0·5 to 1·0 g. of alcohol is mixed in an acetylation apparatus with 10 ml. of a filtered solution prepared by dissolving 50 g. of phthalic anhydride in 250 ml. of pure pyridine, which has previously been dried by distillation in the presence of barium oxide. The reagent should be added as rapidly as possible, *e.g.* from a pipette.

A blank test is made simultaneously, and both reaction-flasks are immersed for 1 hour in boiling water. After addition of 50 ml. of water, immersion is continued for another 10 minutes, and the liquid is cooled and finally titrated with a 0·5 *N* solution of potassium hydroxide in alcohol, with phenolphthalein as indicator; if hydrolysis of the phthalic anhydride is incomplete, acid ethyl phthalates may be formed in alcoholic solutions and lead to erroneous results. Where the acid phthalates have a low solubility (*e.g.* with the sterols), it is advisable to dissolve them in alcohol before carrying out the titration. The percentage of alcohol is then obtained from the formula $M\ (n + ap/28)/20\,pv$, where n is the titre after deduction of the blank; a, the acid value of the substance concerned, using phenolphthalein as indicator; p, the weight in g. of the sample taken; M, the mol. weight of the alcohol; v, the number of alcoholic groups in the molecule. With pure alcohols the formula $n\ M/20\ pv$ may be used. Results are tabulated for 9 samples of primary alcohols or essential oils containing them, and for 22 samples of secondary alcohols. The method is more rapid than the usual procedure (phthalisation in the cold), and is more reliable for certain secondary alcohols (*e.g.* menthol, cholesterol and tetrahydroionol); the presence of sterols, however, interferes with the determination of glycerol, propylene glycol, tartaric acid or benzoin. The rapid identification of alcohols as acid phthalates is illustrated by reference to borneol, a small quantity of sample being heated for 15 to 30 minutes with a 10-fold excess of the phthalic reagent on the water-bath. After addition of a little water and another 10 minutes' heating, the cooled solution is neutralised with potassium hydroxide and then acidified with hydrochloric acid, when bornyl acid phthalate separates; after re-crystallisation from 95 per cent. alcohol, it may be identified by its m.p. (165° C.). The acid phthalates of the tertiary alcohols are obtained more conveniently from the mixed magnesium alcoholates, than from the sodium alcoholates (*cf.* W. A. Fessler and K. L. Shriner, *J. Amer. Chem. Soc.*, 1936, **58**, 1384). It is occasionally advantageous to prepare the silver salts by double decomposition, using silver nitrate, as these compounds are readily re-crystallised from benzene (or precipitated from it by addition of an excess of methyl alcohol) and have sharp melting-points. J. G.

Rapid Saponification of Esters by means of Potassium Hydroxide in Diethylene Glycol. C. E. Redemann and H. J. Lucas. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 521–522.)—Esters and fats can be saponified readily and quantitatively with a solution of potassium hydroxide in diethylene glycol, and usually the alcohol (unless a di- or polyhydric alcohol) can be isolated in a reasonably pure state. Also derivatives of the acid can be prepared in the reaction mixture. Quantitative results cannot be obtained with a volatile inert ester, such as tertiary butyl acetate. Three ml. of diethylene glycol and 0·5 g. of potassium hydroxide are placed in a small distillation flask. After addition of 10 drops of water the mixture is heated until the potassium hydroxide has dissolved. (If the ester to be tested is volatile, the mixture is then cooled.) The ester is added—1 ml. if liquid, 1 g. if solid, or double these amounts if the molecular weight is known to be high. The flask neck is closed with a cork carrying the thermometer and connected by the side-arm with a small condenser. The flask is heated, and its contents

well shaken at the same time, and when there is only one liquid, or one liquid and one solid phase, heating is stopped, and the alcohol is distilled; sufficient is usually collected for the preparation of at least two derivatives. The residue left in the flask is either a solution or a suspension of the potassium salt of the acid portion of the ester in diethylene glycol, and derivatives of this salt may be prepared by adding about 10 ml. of water, 10 ml. of ethyl alcohol, a drop of phenolphthalein solution and 6 *N* sulphuric acid until just acid. The potassium sulphate precipitates in a few minutes and is filtered off, and the clear filtrate may be treated with *p*-nitrobenzyl bromide, *p*-phenylphenacyl bromide or other suitable reagent to give solid derivatives with m.p. useful for identification. Details are given for the preparation of the ethylene glycol solution of potassium hydroxide used in determining the saponification equivalent of the esters; this is carried out by placing 20 to 25 ml. of the reagent in a conical flask, weighing, adding the ester (1 to 3 g.) and re-weighing. The ester is mixed with the solvent by rotating the flask, and while the stopper is held firmly in place, the temperature is raised to 70° to 80° C. in 2 to 3 minutes. The flask is then shaken vigorously, the stopper is loosened and replaced, and the temperature is raised to 120° to 130° C.; after 3 minutes even such refractory esters as dibutyl phthalate are completely saponified. The flask and contents are cooled to 80° to 90° C., the stopper is removed and washed with water, the liquid in the flask is diluted with about 30 ml. of water, phenolphthalein is added, the solution is titrated with 0·5 *N* hydrochloric acid, and the saponification equivalent is calculated in the usual way. A blank test is made by adding the same amount of water to the same volume of reagent and titrating the liquid. D. G. H.

Qualitative Determination of Glycerol and Ethylene Glycol in Dilute Aqueous Solution. A. G. Hovey and T. S. Hodgins. (*Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 509–511.)—Since alkyd resins contain polyhydric alcohols it is necessary in examining such resins to determine the nature of the alcohol, and particularly to find if glycerol is present together with ethylene glycol. For this purpose a colour test has been evolved in which catechol and sulphuric acid are used. The solutions are placed in a 6-in. test-tube in the order named: 3 ml. of the solution to be tested, 3 ml. of a 10 per cent. aqueous solution of catechol (freshly prepared), and 6 ml. of conc. sulphuric acid. The test-tube must be well shaken before the addition of the acid. The mixture is gently heated for about 30 seconds. If glycerol is present, a stable blood-orange colour will quickly appear at about 140° to 145° C. (sensitiveness, 1 part in 700). Ethylene glycol, diethylene glycol and ethyl alcohol give no colour. Other polyhydric alcohols give distinctive colours (given in a table). Since the test for ethylene glycol is negative, confirmation is desirable, and the most distinctive colour differences between this compound and glycerol are given by the polyhydroxy phenols. For example, resorcinol in the presence of sodium hydroxide gives a purple colour with glycerol, and a light green colour with ethylene glycol. When acrolein is substituted for glycerol in the test, a flocculent purple precipitate is obtained. Other aldehydes tend to interfere with the test, but their presence is not likely. It may prove possible to put the test on a semi-quantitative basis. D. G. H.

Shark-liver Oils. M. Tsujimoto. (*J. Soc. Chem. Ind., Japan*, **1937**, **40**, 365B; *cf.* ANALYST, 1935, **60**, 632.)—A further supplement to the author's work on shark-liver oil reports the following data:

Liver oils of:—	Sp.gr. at 15°/4° C.	n_D^{20}	Acid value	Saponification value	Iodine value (Wijs)	Unsaponifiable matter Per Cent.	Crude squalene Per Cent.
1. Aizamé *Centrophorus* Sp.	0·8650	1·4920	0·27	26·2	317·2	86·11	80·7
2. Probably Togaritsuno-,	0·9140	1·4734	0·64	172·0	100·2	7·16	—
zamé	0·9147	1·4735	1·32	174·9	108·3	6·07	—
Squalus japonicus							
3. Aka-ondenzamé Probably *Somniosus microcephalus*	0·9140	1·4738	0·16	161·8	122·1	16·61	—
4. Whale-shark *Rhinodon typicus*	0·9173	1·4750	0·85	187·2	143·0	2·86	—
5. Ôsé or Kirinstobuka *Orectolobus japonicus*	0·9295	1·4815	0·16	182·9	177·0	2·25	—

In every instance the vitamin A content of the oil was far inferior to that of cod-liver oil. Sample No. 4 shows a higher degree of unsaturation in the oil than the sample examined previously, which was obtained from a starved fish (*cf.* ANALYST, 1935, **60**, 633). D. G. H.

Unsaturated Acids of Tohaku Oil. Y. Toyama. (*J. Soc. Chem. Ind., Japan*, 1937, **40**, 285B–289B.)—Tohaku oil is obtained from the seeds of *Lindera obtusiloba*, a plant belonging to the *Lauraceae*; the oil is produced in Chosen. The oil used in these experiments was a dark orange-yellow liquid at the ordinary temperature, and had a terpene-like odour. Its constants were as follows:—sp.gr. at 15°/4° C. 0·9434; n_D^{15} 1·4687; acid value 29·5; saponification value 241·1; iodine value (Wijs) 74·0; unsaponifiable matter (apparently mainly terpenes and resins) 4·67 per cent. Iwamoto (*J. Soc. Chem. Ind., Japan*, 1921, **24**, 1143) found the fatty acids to include capric, lauric, linderic and oleic acids, with probably some lower unsaturated acid. The structure of linderic acid was shown to correspond with that of a $\Delta^{4:5}$-dodecanoic acid (*id.*, 1923, **26**, 708). Subsequently Tsujimoto (*id.*, 1924, **27**, 329) separated a tetradecenoic acid from this oil, which proved to be identical with tsuzuic acid which he had also isolated from tsuzu oil (the seed oil of *Tetradenia glauca*). The author has examined the fatty acids by the usual methods of fractionation of methyl esters, bromination, and oxidation with permanganate, and has confirmed the presence of oleic, linolic, linderic and tsuzuic acids. In addition, he has isolated a decenoic acid with the structure $CH_3{\cdot}(CH_2)_8CH : CH{\cdot}(CH_2)_2{\cdot}COOH$. The tsuzuic acid had the following characteristics:—m.p. 15·5° to 16° C.; sp.gr. at 15°/4° C. 0·9015; n_D^{20} 1·4559; neutralisation value 247·3 (calc. 248·0); iodine value 111·4 (calc. 112·2). E. M. P.

Relation between the Iodine Value and Refractive Index of some Hardened Oils. Y. Maruta and K. Teruyama. (*J. Soc. Chem. Ind., Japan*, 1937, **40**, 299B.)—The relation between iodine value and refractive index for

hardened oils can best be expressed by two different equations giving curves which intersect at an iodine value (I.V.) of about 85. These equations are:

(i) $n_D^{50} = 1{\cdot}4484 + 0{\cdot}000118$ (I.V.) for iodine values above 85

(ii) $n_D^{50} = 1{\cdot}4494 + 0{\cdot}000103$ (I.V.) for iodine values below 85.

The probable error of each equation is $\pm 0{\cdot}0001$ of the refractive index, except for sardine oils having iodine value greater than 85, for which, owing to the complexity of the course of hydrogenation, the probable error is within $\pm 0{\cdot}0004$ of the refractive index. E. M. P.

Extraction of Gossypol with Different Ethers. J. O. Halverson and F. H. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 516–517.)—In the extraction of gossypol from cottonseed meal the best results are obtained by the use of peroxide-free ether containing 2·3 to 2·5 per cent. by weight of alcohol and 1 to 1·2 per cent. of water, and having sp.gr. at 15·6° C., 0·724 to 0·726; the extraction is carried out on a meal containing about 22 per cent. of moisture, in a Soxhlet extractor with a constant bath temperature of 45° C., and 5 ml. of water are added to the ether in the receiving-flask. Ether from which peroxides had been removed was not so satisfactory as peroxide-free ether taken from a drum, owing to the presence of relatively larger quantities of alcohol and water in the drum ether.
D. G. H.

Estimation of Gossypol in Cottonseed Meal. F. H. Smith. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 517–518.)—The moistened cottonseed meal is ground to pass a 20-mesh sieve and well mixed, and the moisture is adjusted to 22 per cent. The meal is extracted for 72 hours with ether, at about 45° C., as described in the preceding abstract. The extract is concentrated to 25 to 30 ml. and filtered through a Gooch crucible containing a layer of "Supercel" placed over a layer of ignited asbestos, and the filtrate is collected in a 200-ml. Erlenmeyer flask under a bell-jar, in the top of which is a hole for a cork holding the stem of the Gooch holder and a glass tube to which suction is applied. The flask and crucible are rinsed with ether, and the rinsings are added to the filtrate. The ether is removed from the flask by applying suction and rotating the flask in water at a temperature not exceeding 50° C. When rapid boiling stops, 75 ml. of petroleum spirit and 5 ml. of ethylene glycol are added, and the contents of the flask are mixed and left overnight. The precipitated material is filtered off (as described above), and the precipitate is washed with a small amount of petroleum spirit, the temperature of filtrate and washings being kept about 35° C. to prevent further precipitation. Two ml. of aniline are then added, and the flask is shaken and left for 1 to $1\frac{1}{4}$ hours in hot water (50 to 55° C.) not exceeding 2 in. in depth. The volume is then made up to 50–60 ml. with petroleum spirit and the flask is left overnight. If the precipitate is small (10–15 mg.) the flask is left for at least 36 hours. The precipitate of dianiline gossypol is collected on a weighed Gooch crucible, washed four times with water, followed by 5 ml. of 95 per cent. alcohol and a few ml. of petroleum spirit. It is dried to constant weight at 100° C., and the weight is multiplied by 0·775 to obtain the equivalent weight of gossypol. D. G. H.

Characteristic Reaction of Yperite. B. Jélinek. (*Bull. Soc. Chim.*, 1937, **4**, 1813–1815.)—A strip of filter-paper is immersed in an ammoniacal solution of silver hydroxide and then in a fresh solution of a little isatin in 1 to 3 ml. of concentrated ammonia; it is finally dried in air. If this strip is placed in contact with a drop of yperite a yellow colour appears, surrounded by a dirty deep green halo. The former colour is due to decomposition of the reagent, and the latter to the superposition of the above-mentioned yellow colour, the Bordeaux-red colour of the reagent, and the blue colour of the indigoid type of compound formed by the condensation of two silver-isatin complexes under the action of the chlorine atoms of the yperite. The colour takes 1 hour to develop at room temperature, but if the paper is warmed to 60° to 80° C. by holding it against the surface of a glass vessel containing hot water, only 1 minute is required. If the remainder of the indicator on the test-paper is decomposed by means of a mixture in equimolecular proportions of acetic acid and ethyl alcohol, a deep blue circular stain results, which is very stable even towards light. The reaction may be used for liquid yperite or for solutions (*e.g.* in benzene), but it has not been tested with yperite in air. The reagent is stable towards light, but is decomposed by, or else insoluble in, organic solvents, and it is sensitive to changes in *p*H value. J. G.

Composition of Coconut Shells. L. C. Fleck, W. G. Van Beckum and G. J. Ritter. (*J. Amer. Chem. Soc.*, 1937, **59**, 2279–2280.)—Analysis of coconut shells by the standard methods for hardwoods yielded the following results, based on the weight of oven-dry (105° C.) shells:—moisture, 6·07; cold-water-soluble substance, 1·43; hot-water-soluble substances, 2·67; ether-soluble substances, 0·19; soluble in 1 per cent. alkali, 20·53; lignin, 33·30; total pentosan, 30·28; ash, 0·23; holocellulose, 61·00; cellulose, 44·98; pentosans in cellulose, 17·67; pentosan in cellulose, 39·30*; (loss in cellulose due to hydrolysis by 15 per cent. H_2SO_4, "Hydrolysis No.," 35·85)*; cellulose stable to hydrolysis by 15 per cent. H_2SO_4, 28·86; methoxyl, 5·39; acetic acid by hydrolysis, 4·79; loss in weight of shells on hydrolysis by 2·5 per cent., H_2SO_4 (in acetic acid determination), 18·74.

The yields of lignin, total pentosans and pentosans in the cellulose are higher in the shells than in hard-woods, but the percentages of cellulose, cellulose stable to hydrolysis by 15 per cent. sulphuric acid, and holocellulose are considerably lower than those from woods. The methoxyl and the acetic acid contents are about the same in shells and woods. E. B. D.

Preparation of Phosphomolybdic Acid Reagent. S. L. Malowan. (*Z. anal. Chem.*, 1937, **111**, 7–10.)—The following method for preparing phosphomolybdic acid for use as a reagent for alkaloids, etc., is recommended:—Ammonium phosphomolybdate (5 g.) is heated in a porcelain crucible, the bottom of which is kept at a dull red heat. When the yellow precipitate has been completely converted into a bluish-black mass, this is cooled and boiled with about 20 ml. of 3 per cent. hydrogen peroxide until dissolved to form a golden-yellow liquid. The clear solution is evaporated with a few drops of nitric acid, and the residue, when dissolved in a suitable volume of water, furnishes the reagent.

W. R. S.

* On the basis of Cross and Bevan's cellulose.

Inorganic

Reduction of Ferric Salt by Metallic Tin. R. Rinne. (*Z. anal. Chem.*, 1937, **111**, 1–3.)—The reduction of ferric salt by metallic tin instead of stannous chloride solution prior to titration is convenient. The acid chloride solution, to which a piece of pure tin has been added, is boiled until colourless, after which boiling is continued for one, or at most two, minutes. The beaker is then cooled in water, the tepid solution is decanted into another beaker, and the tin is washed three times, the washings being added to the reduced solution. This is treated with mercuric chloride, etc., in the usual manner. W. R. S.

Measurement of Thickness of Tin Coating on Steel by a Magnetic and an Electro-magnetic Method. B. Chalmers, W. E. Hoare and W. H. Tait. (*Tech. Pub. Int. Tin Research and Dev. Council*, 1937, Series A, No. 66.)—*Magnetic Method* (*J. Scientific Instruments*, 1937, **14**, 248).—This method enables the coating-thickness to be determined virtually at a point, and is thus of service in exploring the surface of tinplate for small-scale variations in thickness of the tin layer. The method depends on measuring the force required to detach a small permanent magnet from the surface. This force is a linear function of the thickness of coating. The apparatus consists of a beam supported approximately at its centre of gravity on steel points. At one end of the beam is a counterpoise, and at the other end is a small bar magnet with a cylindrical pole-piece. In the "on" position, the pole-piece adheres magnetically to the surface of the specimen rigidly supported underneath it. Attached to the beam in a vertical position above the magnet is a glass test-tube provided with a scale and containing water, the quantity of which can be varied by siphoning until the magnet becomes detached from the surface of the specimen. The level of water can be read on the scale, which can be calibrated to indicate thickness of coating.

Electromagnetic Method (*J. Scientific Instruments*, 1937, **14**, 341).—The measuring unit is a small transformer, and, when in use, the magnetic circuit comprises the core, the basis steel, and the gaps formed by the non-magnetic tin coating. The output of the transformer, which can be measured by a suitable instrument, depends on the width of the gaps, and therefore on the thickness of the coating. This method is said to be more suitable than the preceding one for workshop use for measuring average thickness and large-scale variations in thickness. S. G. C.

Determination of Small Amounts of Beryllium in Aluminium Alloys. E. Pache. (*Chem.-Ztg.*, 1937, **61**, 880).—A 5-g. sample of the alloy is dissolved as far as possible in 100 ml. of 10 per cent. sodium hydroxide solution; 600 ml. of hot water are added, and the liquid is kept hot for half-an-hour. The beryllium remains in the undissolved residue together with iron, manganese, magnesium, titanium, chromium, and a little undissolved aluminium and zinc. The precipitate is filtered off, washed with cold water, and dissolved in 20 ml. of hot dilute nitric acid. The solution is slowly added, with shaking, to 100 ml. of freshly prepared 40 per cent. sodium hydroxide solution, the liquid is diluted to 500 ml., and an aliquot portion, containing beryllium, aluminium and zinc, is filtered off. The

filtrate is acidified with nitric acid, and the beryllium and aluminium are precipitated as hydroxides by means of ammonia. The precipitate is filtered off, washed with cold water and dissolved by heating in 5 ml. of 10 *N* potassium hydroxide. The solution is diluted with 500 ml. of water, and the liquid is boiled for 40 minutes to precipitate the beryllium hydroxide. The precipitate is allowed to settle out by keeping the liquid hot for some time, filtered off, washed with warm water, ignited and weighed as beryllium oxide. S. G. C.

Determination of Silica in Acid-soluble Silicates. W. v. Tongeren. (*Chem. Weekblad*, 1937, **34**, 774–777.)—Comparative tests of various methods of determining silica in acid-soluble samples are described. The following method has been found a good one. A 1-g. sample of the finely powdered substance is mixed with 1 g. of ammonium nitrate in a small Jena-glass beaker; 5 ml. of nitric acid (sp.gr. 1·4) are added cautiously, and the beaker is covered with a watch-glass and heated on a water-bath for half-an-hour, the contents being frequently stirred. The silica is then filtered off on a filter, upon which a little macerated filter-paper has been placed, and is washed with 100 to 125 ml. of hot 5 per cent. nitric acid containing a few drops of hydrogen peroxide. The silica is thus obtained practically quantitatively in a very pure condition and is determined in the ordinary way. S. G. C.

Phosphorus Pentoxide as a Desiccant at 90° C. D. A. Lacoss and W. C. Menzies. (*J. Amer. Chem. Soc.*, 1937, **59**, 2471–2472.)—A current of air was passed at the rate of about 650 ml. per hour through a series of vessels containing the following reagents:—(1) calcium chloride, (2) sulphuric acid (aqueous pressure about 1 mm.), (3) phosphorus pentoxide at 90° C., (4) magnesium perchlorate, (5) phosphorus pentoxide, (6) guard-tube. All the reagents except (3) were at room temperature. During 35 days more than 0·5 g. of moisture entered (3), but there was no change in weight in (4) or (5). Within the experimental error, phosphorus pentoxide is as efficient a desiccant at 90° C. as at room temperature. If a gain in weight up to 0·5 mg. was unobserved, the aqueous pressure of the air which passed (3) did not exceed by more than 0·0009 mm. that of the air which passed (4) and (5). E. B. D.

Microchemical

Microchemical References. (*Mikrochimica Acta*, 1937, **1**, 106–119, 231–248, 300–312, 366–378 ; and **2**, 155–174, 242–272.)—References to the current literature, with titles, are given under the following subject headings :—I, Inorganic (preparative and analytical) chemistry. II, Physical and physico-chemical methods. III, Organic chemistry (preparative and analytical). IV, Biochemistry (animal and human). V, Medico-chemical methods. VI, Plant physiology, agricultural chemistry, food chemistry and allied subjects. VII, Pharmacy, toxicology; forensic chemistry and allied subjects. VIII, Applied chemistry (technical chemistry, mineralogical chemistry, etc.). IX, Apparatus.

Collected References. Quantitative Micro Mineral Analysis. F. Hecht. (*Mikrochimica Acta,* 1937, **2**, 120–154.)—A critical summary is given of the 40 different publications on this subject, all of which have appeared in the past 10 years. The pioneer work of Benedetti-Pichler and co-workers on the analysis of the beryllium silicate rocks is described in detail. These authors use the filter-stick technique with gravimetric analysis, chiefly using low temperatures for drying precipitates and avoiding ignition. A gravimetric method for the determination of water in coal and other solids is described. Complete micro analyses have been carried out on radio-active minerals (with special reference to lead, uranium and thorium). Fifteen constituents were determined in some samples, giving values 99·56 per cent., 101·70 per cent., and 98·98 per cent. for the sum. Different uraninites and monazite and many other minerals have also been analysed. Various methods, direct and indirect, are given for silica. One very recent analysis is mentioned in which SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O^{-}*, H_2O^{+}*, CO_2, TiO_2, P_2O_5, SO_3, and MnO are all determined on the micro-scale by the methods of Hecht and his co-workers. Methods are briefly described for the determination of water and of ferrous iron. J. W. M.

Detection of Organic Compounds by means of Spot Tests. F. Feigl. (*Mikrochimica Acta,* 1937, **1**, 127–141.)—Various spot reactions for the detection of small amounts of organic compounds are cited. New spot tests for the detection of the following atomic groups and compounds are described:—(1) *Sulpho- and sulphonic acids.*—The alkali sulphite formed by fusing the sample with caustic potash is identified. Details of this test are now available in text-book form (Feigl, *Qualitative Analysis by Spot Tests: Inorganic and Organic Applications.* Trans. 1937, Amsterdam and New York, p. 275). (2) *Hydroxylamine and Oximes.*—These are oxidised by means of iodine to nitrous acid, which is detected by means of Griess's reagent. (3) *Aryl hydrazines, hydrazones and osazones.*—These are oxidised by means of selenious acid to a diazonium salt which, in turn, is coupled with α-naphthylamine; details available in text-book form (*loc. cit.*, 289–290). (4) *Glycerol and glycerides.*—These are converted into acrolein, which is detected by means of sodium nitroprusside and piperidine or by means of *o*-dianisidine (*loc. cit.*, 308). (5) *Aliphatic secondary amines.*—These give a colour reaction with sodium nitroprusside and acetaldehyde (*loc. cit.*, 280). J. W. M.

Microchemical Reactions of Sparteine with Cobalt and Iron Salts. A. Martini. (*Mikrochimica Acta,* 1937, **1**, 164–167.)—Cobalt thiocyanate solution (10 g. of cobalt nitrate and 10 g. of potassium thiocyanate dissolved in 30 ml. of warm water) is a characteristic reagent for sparteine and is capable of detecting 1γ. On mixing a drop of the reagent with a drop of an acid solution of the alkaloid (sparteine hydrochloride or sulphate) a blue precipitate is formed which is of the same colour when viewed through the parallel nicols and appears as strongly doubly diffracting when the nicols are crossed at an angle of 15°–20°. Two photomicrographs are given to show the appearance. The crystals formed with nicotine under the same conditions are completely different. In dilute

* These signs indicate water expelled below and above 110° C. respectively.

solutions only sparteine reacts. Alternatively, the reaction may be used as a test for cobalt salts; as reagent 40 g. of ammonium thiocyanate and 5 g. of sparteine sulphate are dissolved in 100 ml. of water. On treating a drop of a 1 per cent. solution of a cobalt salt with this reagent the characteristic blue crystals are formed. Zinc and cadmium salts give a white precipitate, copper salts a brown precipitate. Ferric salts, after some time, form orange-red crystals, but badly shaped. Better crystals are obtained by treating the ferric salt with propionic acid (1:2) or hydrochloric acid, followed by perhydrol, and then with the reagent. These crystals are characteristic under the polarising microscope; two photomicrographs are shown. In this way as little as 0·01γ of iron may be detected. J. W. M.

Applications of a Sensitive Test for Alkali. Y. Kondo. (*Mikrochimica Acta*, 1937, **1**, 154–159.)—The reaction between manganese salts, silver salts and alkalis, $2Ag^{\cdot} + Mn^{\cdot\cdot} + 4OH' = 2Ag + MnO_2 + 2H_2O$ may be applied, according to Feigl ("*Quantitative Analysis by Spot Tests*," 1937), to the detection of manganese or silver or alkalinity. The oxides and carbonates of the alkalis and alkaline earths react with the silver-manganese reagent; thus, the reaction is suitable for testing the alkalinity of ash from paper and from coal, for testing soaps, for investigating the alkali liberated from glass, and further for determining the hardness of water. *Reagent solution.*—2·87 g. of manganese nitrate are dissolved in 40 ml. of water and a solution of 3·39 g. of silver nitrate in 40 ml. of water is added. The mixture is diluted to 100 ml., and dilute alkali is added until a black precipitate begins to form. This is filtered off, and the solution will then keep in the dark. Paper-ash is tested after ashing a small strip (2 $\times$ 3 mm.) in a porcelain crucible lid. On the addition of a drop of reagent the ash turns black or grey, either at once or after a few minutes, according to the alkalinity. Cigarette-paper, newspaper and writing-paper give a strongly alkaline ash. The hair-like structure of the paper-ash is much more readily seen under a microscope ($\times$ 100) after carrying out this test. For testing coal-ash, samples of 0·1 g. of coal are ashed. Various coals may be differentiated by the reaction of either the ash or the water-soluble ash. For testing the various types of glass the samples are ground for similar periods of time in an agate mortar, and the powder is stirred with a drop of the reagent solution. The intensity of blackening is noted after a few minutes. Scarcely any reaction was obtained with Jena-Duran glass and Pyrex glass; Kavalier glass and various optical glasses gave the strongest reaction. For water-testing, the dried residue of a single drop of water (0·05 or 0·01 ml.) is tested with the reagent. An etched slide is best for this test, as it renders it easier to keep the areas of the evaporated drops equal. The intensity of blackening is compared with a standard. In testing soap for excess of alkali a drop of the reagent solution is applied to the freshly cut surface of the sample. Positive reactions were obtained with various soaps after 1 to 20 minutes. A slight reaction (*i.e.* after 10 to 20 minutes) indicated that there was no excess of alkali. J. W. M.

Detection and Estimation of Minute amounts of Fluorine by the Etching Test. E. R. Caley and J. M. Ferrer, Jr. (*Mikrochemica Acta*, 1937, **1**, 160–163.)—The etching test, as normally used, is unsuitable on the micro-scale,

as it is insufficiently sensitive, owing to the use of apparatus of large internal volume, leakage of evolved hydrogen fluoride, the use of wax on the glass surface, and making the test at too low a temperature. An improved apparatus consists of a cylindrical piece of lead about 3 × 3·5 cm., in which is cut a cylindrical hole, 1 cm. in diameter and 2·5 cm. deep. A 1-cm. flange is provided, 0·5 cm. from the top of the lump of lead, cut so that the apparatus can be handled with a pair of tongs, and may be placed in a ring of an oil-bath or metal heating-block. The top surface, surrounding the hole, is ground flat to take a microscope cover-glass, and a heavy lid of lead fits over the top and reaches nearly down to the flange. Various weights of calcium fluoride were placed in the cavity of this apparatus, and covered with 1 ml. of 95 per cent. sulphuric acid, and tests were made at various temperatures. At room temperature, or slightly higher, poor results are obtained. Even at 110° to 115° C., excessive time is required to obtain satisfactory results, whilst at 150° C. the time is much shorter. The optimum temperature appears to be 150° C., or slightly higher, but well below 175° to 200° C., to avoid the fuming of the sulphuric acid. At 150° C., 0·05 mg. of calcium fluoride may be detected after 30 minutes. The etched cover-glasses provide a convenient permanent record; under exactly the same conditions the amount of etching is roughly proportional to the amount of fluoride. J. W. M.

Physical Methods, Apparatus, etc.

Use of Acridine Orange and Brilliant Diazol Yellow as Fluorescent Indicators. M. Déribéré. (*Ann. Chim. anal.*, 1937, **19**, 290–291.)—Various commercial samples of acridine orange (Colour Index No. 788) show a change in fluorescence from bright orange at *p*H 8, to yellow at *p*H 10 to 10·5 (*cf.* Jensen, ANALYST, 1933, **58**, 722). Oxidising and reducing agents are without appreciable effect on the change, although the colours seen are duller. In alkaline solutions brilliant diazol yellow has a violet-blue fluorescence, which disappears between *p*H 6·5 and 7·5; if the solution is very dilute, the fluorescence in alkaline solutions is green, or even yellow. Reducing agents displace the end-point towards a higher *p*H value, whilst oxidising agents destroy the fluorescence completely. J. G.

Reviews

A HUNDRED YEARS OF CHEMISTRY. By ALEXANDER FINDLAY, D.Sc., Ph.D. Pp. 352. London: Duckworth. 1937. Price 15s. net.

Chemistry, as an exact science, came into being towards the opening of the nineteenth century, through the systematic application of quantitative measurements to chemical phenomena. These measurements depended largely, although not solely, upon the use of the balance. The three chief pioneers in the effective scientific use of this instrument were Black, Cavendish, and Lavoisier. Dalton's Atomic Theory (1807), the logical outcome of the quantitative chemical work of the late eighteenth century, was consolidated by the later determinations of Berzelius, one of the greatest of all protagonists of the balance. Berzelius also showed (1815) that organic compounds could be represented by means of

molecular formulae; and soon afterwards organic chemistry began to assume the status of an exact science, when Liebig (1831) improved Berzelius' original method of elementary organic analysis.

Such was broadly the position which chemistry had reached a century ago, when Professor Findlay's narrative begins. It is now evident that the time was ripe for a rapid advance upon an ever-widening front, but no contemporary chemist could have foreseen, even dimly, the rapidity of that advance, or the vast dimensions which that front was to assume a hundred years later. How one would like to borrow for a while a Time Machine which would enable one to deliver a copy of Prof. Findlay's book into the eager hands of Berzelius, Liebig, or Laurent, and to savour the reaction of the recipient! We can imagine no better medium for such an intriguing orientation of these paladins of the past; nor can we conceive of a better one for the less intriguing but more practical purpose of showing the average chemist of to-day how his science has developed during the past hundred years and where it now stands.

The whole story has been skilfully compressed within the compass of some three hundred pages. Here the reader with a grounding in chemistry will find related in broad outline the development of inorganic, physical, and organic chemistry, and of more specialised aspects of pure and applied chemistry, such as stereochemistry, radio-activity, and the chemical industry founded upon coal-tar. There are numerous references to original papers, and the author has achieved a high degree of accuracy. The last twenty pages of the text are devoted to short biographical notes on eminent chemists who figure in the narrative, and there is a good index of fourteen pages. The book is printed in a large clear type and is well produced. The illustrations are confined to a few simple line diagrams and tables.

JOHN READ

THE ANALYTICAL CHEMISTRY OF TANTALUM AND NIOBIUM. W. R. SCHOELLER, Ph.D., F.I.C. Pp. xvi + 198. London: Chapman & Hall, Ltd. 1937. Price 21s.

This book marks an epoch in the history of the Society, inasmuch as it is the first one to be published under its auspices, which fact is signalised by a foreword contributed by the President; it sets a high standard to any possible successors. The number of people who are directly concerned with the determination of tantalum and niobium must be remarkably small, and of these, the great majority, probably the whole, must be very well acquainted with Dr. Schoeller's work, for the simple reason that they cannot adequately carry out these determinations without reference to it. On this account it might seem probable that this valuable book would have a very much more restricted circulation than its merits demand; this would be a pity, for its message goes very far beyond the limited bounds indicated in its title. No man can spend the many years which the author has spent in doing research on elements with such a pronounced tendency as tantalum and niobium to form colloidal precipitates, without acquiring deep-rooted notions on the subject of colloidal precipitates generally; therefore all those chemists who are in the habit of trying to dissolve one constituent out of a mixed colloid precipitate (say antimony sulphide from a mixed sulphide precipitate)

would do well to see what he has to say on the subject. Also, even if tantalum and niobium have not as yet found widespread uses, the same cannot be said of titanium, tungsten and zirconium, and these elements with others figure largely in the book.

The contributions which Dr. Schoeller and his numerous collaborators have made to the analytical chemistry of the elements included in his title are now a matter of history, and no one will question his authority; it must have been a temptation, however, to an author who has published 33 papers on a subject and afterwards writes a book about it, to make that book largely a compilation or re-hash of the papers. It may be said at once that if this temptation existed, it has been successfully resisted, and the result is a well-balanced and very readable book. Those chemists who are directly concerned with determining tantalum and niobium must often have felt the strain of searching through the many papers published by Dr. Schoeller and been possessed sometimes by an uneasy feeling that they might have overlooked some vital factor. The final summary (No. xxxiii) did not entirely remove this difficulty. They now have, within the covers of this book, a complete account—not qualified by something which has gone before, nor likely to be modified by something which may follow—on which they can base their work with confidence. The treatment of tantalum and niobium is as complete as can be desired; it includes separation from other elements (tungsten, titanium, and so on), as well as from one another.

As stated above, the ordinary inorganic chemist will find much that will interest him; for instance, the separation of zirconium, uranium, aluminium, and beryllium (p. 135 *et seq.*), the separation of beryllium from a large number of metals (p. 154), and of titanium from another series (p. 153), and the quantitative precipitation of ten metals from neutral tartrate solution. Some 24 pages (*i.e.* one-eighth of the whole) are given up to the use of tannin as a reagent in mineral analysis generally; in this section tantalum and niobium occur only as two members of a fairly large family. The work ends with a chapter on the qualitative detection of tantalum and niobium and one on the literature of earth acid analysis containing a classified list of the papers published by Dr. Schoeller and his collaborators.

The book is attractively bound and exceedingly well printed, and only one misprint was noticed; an unusual feature is the very thick paper employed, resulting in a presentable volume whose pages are easily turned. Dr. Schoeller and what he calls "the team" he has "captained" are in a sense a band of explorers who for years have been struggling through the jungles of an almost untrodden country. The papers published are so many bulletins issued, often when the explorers could not see over the next ridge. This book is the final account of a surveyed and mapped territory.

B. S. EVANS

BENTLEY AND DRIVER'S TEXT-BOOK ON PHARMACEUTICAL CHEMISTRY. Third Edition. Revised by J. E. DRIVER, Ph.D., M.Sc., F.I.C. Pp. ix + 624. London: Oxford University Press. 1937. Price 16s. net.

The third edition of this book has been rendered necessary by the publication of the 1936 Addendum to the 1932 Edition of the British Pharmacopoeia. The book consists, as did its predecessors, of an introduction, a section on analytical

methods, one on inorganic compounds, one on organic compounds, and an appendix. The addition of substances included in the Addendum to the Pharmacopoeia is the main difference between this and the second edition.

Dr. Prideaux has again written that part of the book dealing with hydrogen-ion concentration and the methods for determining it.

While it is admittedly a difficult task to write a book of pharmaceutical chemistry which can be used by the average student of pharmacy, it is doubtful whether abbreviated descriptions of general methods of analysis should be included, or whether the student should not be referred to the relevant text-books on practical chemistry. For instance, a description is given of the method for determining halogens in organic compounds by means of the Carius tube, and yet no official substance is assayed by that method. Again, in a description of the Kjeldahl method for the determination of nitrogen, no mention is made of accelerators, and yet when the analysis of malt extract is discussed it is stated that the Kjeldahl method is used for determining the nitrogen, and that copper sulphate may be used as an accelerator.

One very curious statement appears on page 14, where it is stated that "for convenience, one-hundredth of a poise is called a centipoise and one-hundredth of a stoke is called a centistoke." Presumably, if it were not convenient to do so, one-hundredth part of a metre would not be called a centimetre.

Some of the diagrams are rather antiquated, although others are quite up-to-date. As a text-book for students of pharmacy who are preparing for the chemist-and-druggist qualification, the work can be recommended. S. G. STEVENSON

DRUGS AND GALENICALS: THEIR QUANTITATIVE ANALYSIS. By D. C. GARRATT, B.Sc., Ph.D. (Lond.), F.I.C. Pp. 400. London: Chapman & Hall, Ltd. 1937. Price 25s.

The author of this work has arranged the text in a series of monographs, in alphabetical sequence, which set forth the methods of examination used in the very wide field of quantitative analysis of drugs and medicines.

Of necessity, he has been obliged to follow the processes and details provided in the pharmacopoeias official in this country and abroad, but these are amplified by the more recent work published in scientific journals concerned with the subject of drug analysis, to which numerous references are given in THE ANALYST and the abstracts from other journals.

Upon such a subject there is constant need for analysts to refer to the published work of the most recent investigators, and Dr. Garratt has collected this work comprehensively and successfully in one volume.

It is impossible to criticise the book in detail, for each monograph might be discussed page by page. In considering such a work as this it is important to bear in mind that each and every subject dealt with has been the subject of lengthy and competent discussion, and hence the value of the book as a compendium of tried methods of analysis for the assistance of analysts in general, and in particular those working in pharmaceutical laboratories.

The monographs deal with nearly every drug in the British Pharmacopoeia and the methods of analysis of each and its preparations, and it must have

necessitated much careful investigation and trial to eliminate some of the ancient methods, which have been proved to be either erroneous or unreliable.

Such subjects as opium, ergot, cinchona, henbane, ipecacuanha and coca, may seem beyond the possibility of revision, but even for those the author has found additional details for inclusion in the many pages of description. Such drugs as derris, ephedra, pyrethrum and santonica have brought quite new material to the book.

The sections dealing with mercury, lead, zinc and copper, include the most recent technique and the application of organic reagents to the detection and estimation of minute quantities of these metals.

The synthetic drugs are subjects of particular importance, especially such as acetanilide, phenacetin, phenazone, salol and amidopyrin. For these the author gives reliable methods, and although some of them are not novel, yet they deal with the analysis of compounds very frequently met with in pharmacy and used for tablet medicaments. The A.O.A.C. methods occur frequently.

Particular interest attaches to the section on arsenic, the methods being described and an account given of the organic arsenicals now in use by physicians.

The barbituric compounds are of such importance that an extension of this monograph would be of service in a future edition.

Dr. Garratt has summarised his own work and experience with oils, fats, waxes, soap and essential oils, and by grafting it on to the standard methods of other workers, and those of the Essential Oil Sub-Committee of this Society, he has compiled two most useful chapters, which summarise most of the recent work, on these subjects. The tables of constants for both fixed and volatile oils are particularly useful for general reference.

The determination of the proportions of volatile oils in drugs and spices is receiving much attention from the compilers of Continental pharmacopoeias, and will be considered more often in future by the Public Analyst at home. Cocking and Middleton's apparatus for obtaining the volatile oil from small quantities of material is illustrated, and their recently published results are given *in extenso*, as well as a tabulated list of drugs yielding them, and the proportions given in the latest edition of the B.P. Codex.

The book contains a number of useful appendixes dealing with special matters of general interest, such as, for example, the determination of moisture by distillation with immiscible liquids; a method for the routine determination of traces of metallic impurities; the Stas–Otto method for extracting poisons from viscera; the methods for determination of alkaloids; determination of alcohol-content, and tables of the alcoholic strengths of official tinctures and pharmacopoeial preparations; Skalweit's glycerin tables, and Lane and Eynon's sugar tables. These, with others, make the book a most useful companion for any busy analyst, and will save a vast amount of time by affording references to original work scattered throughout a multitude of current publications.

The book is well arranged and the proof-reading must have been exhaustive, or the printer particularly efficient. The water-proof binding will allow the book to be used in the laboratory without undue risk, and it is safe to predict that, by reason of the strong sewing into the back, the sections will not part from the covers.

C. EDWARD SAGE

Perspectives in Biochemistry. Thirty-one Essays Presented to Sir Frederick Gowland Hopkins by Past and Present Members of his Laboratory. Edited by Joseph Needham and David E. Green. Pp. 350. Cambridge: University Press. 1937. Price 15s. net.

One of our leading biologists has told me of a discussion, some years ago at the British Association, when a zoologist of distinction ventured once more to posit the very old question, "What is a species?" and himself supplied an answer that raised appreciative chuckles among those whom the question had vexed for so long. "A species," he said, "is a group of plants or animals that has been defined as a species by a competent taxonomist."

The subject continued, as usual on these occasions, to be canvassed in hotels and restaurants and soirées and conversaziones—with, so my informant insisted, the result that what had first been taken as a rather attractive wisecrack, came soon to be regarded as the best answer to the question that most of those present had heard. At least, it had one completely satisfactory feature: it recognised to the full that man's artificial and arbitrary way of drawing lines on the face of young Nature can have only one justification, that they serve the purpose for which they were intended. As usual, an ounce of empiricism is worth a ton of *a priority*.

Biochemists in these days are beset from two sides. The organic chemist says, "You can't do without me; by curious, rather shady, methods of your own—methods that no real chemist would tolerate—you extract from plants or animals, or rather from the dead shells of what had once been plants or animals, certain crude substances which you then pass to me to be examined by truly scientific methods. When I have purified, analysed and synthesised something from the mess, I return it to you, and I haven't the least idea what happens to it next. All I *do* know is that until I appear on the scene, nothing worthy of the name of science has been applied to the substances in question. So much for biochemistry."

When the purified substance has duly been handed to the physiologist, the pharmacologist and possibly even the clinician, the attack from the second side begins. The biochemist is, perhaps, thanked for his services in acting as middle-man between these workers and the organic chemist, but it is, not too delicately, hinted to him that biological science and the art of medicine have as little use for him as had organic chemistry. "So much for biochemistry!"

When, therefore, the biochemist is asked the recurrent question: "What is biochemistry?" he tends to feel that he and his subject are almost as undefinable as a species. Yet there is an answer to the question, a simple, useful and incontrovertible answer. It is given not so much by the contents of "Perspectives in Biochemistry" as by the very origin and existence of the book. Biochemistry, it may be said, is that blend of biology and chemistry, in whatever proportions, that is practised jointly and severally by Sir Frederick Gowland Hopkins and any or all of those who have been directly or indirectly influenced by him. There you have a definition both comprehensive and exclusive.

This book, presented to Professor Hopkins on the occasion of his 75th birthday by past and present members of his laboratory, is possibly the first "*Festschrift*" produced and published in this country; it is certainly the first biochemical

"*Festschrift*," although, as a colleague of mine has remarked acidly: "the editors and publishers are to be congratulated on having nowhere referred to this volume as a '*Festschrift*'." Nevertheless, it is exactly that. In this book, then, one will expect to find one's definition exemplified or overturned: the reader must decide which. True, there is a great deal of organic chemistry, much physiology, some comparative anatomy, and even more than a smattering of physics. Yet is it not clear that the biochemists have, for example, taken over from the physiologists methods of studying cell metabolism, have brought to bear on those methods a knowledge of organic chemistry, particularly of the hydroxy and ketonic fatty acids, have introduced, moreover, the technique of the analytical chemist, and have thus integrated a procedure of investigation that may or may not merit a new name, but that has assuredly given new information?

Of all the thirty-one essays in this book, the one that seems to me most completely satisfying, and to respond best to the editors' bidding to write something "suggestive and provocative," is that by Professor Szent-Györgyi, this year's recipient of the Nobel prize for medicine. His brilliant and convincing little masterpiece is as happy a blend as could be wished of the deduction that comes legitimately from accurate experiment, with the speculation that is directed to experimental results by a shrewd and philosophical mind. Szent-Györgyi's essay makes simple a complex and baffling problem, with no sacrifice of accuracy or importance.

Many of the essays in this book cover familiar ground, but mostly in a more or less novel way, as befits the occasion. Dr. Pirie's ingenious and disarming paradox must be read to be believed—but he really does seem to prove that the one concept foreign to the aims of the biochemist is that of life and living. Professor Edward Mellanby returns to battle on behalf of the rachitogenic toxamins, and is even willing to sacrifice the neurotoxic one, if he may have his anti-calcifying factor saved from the cereal wreckage. The objective and restrained spirit, however, in which he defends his thesis, always prepared to submit ultimately to the test of laboratory practice and clinical experience, shows again the immanence of the Hopkins outlook and reminds us that Professor Mellanby, too, is to be counted among those who once lived in Arcadia and who have never forgotten it.

There is much less about vitamins in this book than might have been expected, seeing how closely the name of Hopkins is associated with the subject. In a discussion on vitamin C and infection, Dr. Leslie Harris insists on keeping open a number of explorable avenues, and it is much to be hoped that he will long continue to be in the exploring parties, for his wide reading, enthusiasm and humanitarian outlook are valued supplements to his scientific skill and integrity; and all of these are needed in any one who proposes to extend the investigation of infection beyond the realms of bacteriological taxonomy.

Professor Friedmann contributes the only other essay bearing directly on vitamins. His discussion on vitamin D makes clear the essential relationship between a certain chemical structure and the property of convertibility into an antirachitic compound, as well as the relationship between another derived chemical structure and the actual physiological properties of vitamin D. These relationships follow from the recent chemical investigations that are adequately summarised by

Professor Friedmann, who, however, has unfortunately failed to correct the provisional data on crude vitamin D_3 by the more recent information that must have been accessible many weeks before his essay went to press. One or two other inaccuracies in Professor Friedmann's article—such as the spelling of the names of McCollum and Heilbron—are minor blemishes in a useful summary.

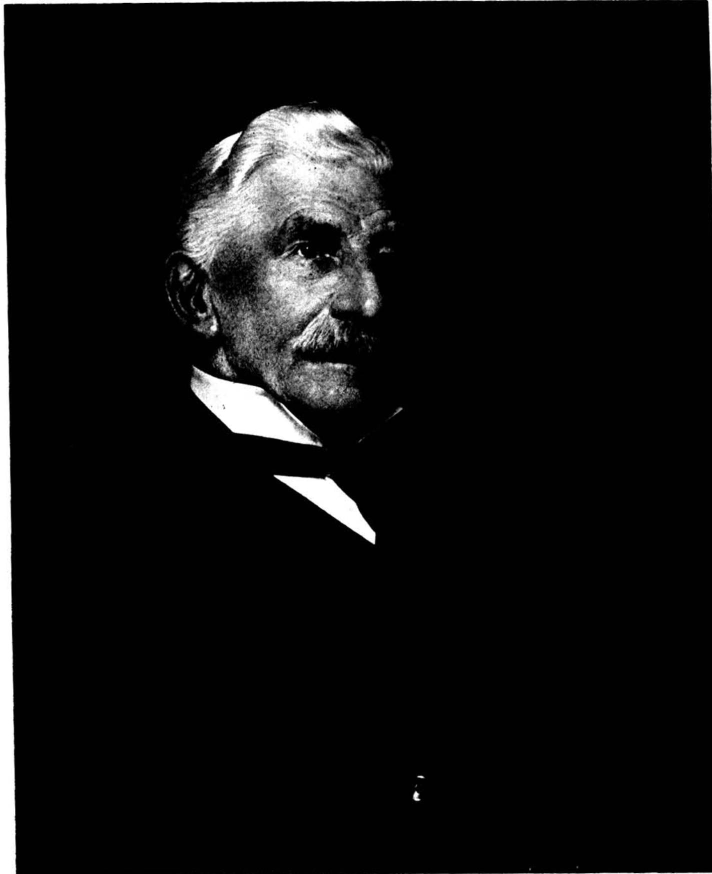
It would be easy, and for the reviewer very pleasant, to comment in turn on every one of these fascinating extrapolations from current knowledge, but there are limits to the patience of readers as well as to the forbearance of editors. The intellectual prowess of Professor Haldane and Dr. Bernal has nowhere shown to greater advantage than in their respective contributions to this book. It is curious, however, that the former should write a virile and almost impeccable English, while the latter has a prose style that is ungainly to the point of inaccuracy. At least two of Dr. Bernal's sentences are palpably ungrammatical, and one would venture to plead with him to cease to be the exception that proves an old-established rule—that incorrect syntax is a symptom of faulty logic.

The reader in search of unexpected and astonishing facts will find plenty in the essays by Dr. Wigglesworth, Dr. Quastel, Dr. Needham and others. For an example of defence so rigorous as to pass almost into its opposite, the essay of Professor Raistrick is to be commended to chemists in particular. One hesitates to describe it as truculent, but there is surely no mistaking the North Country origin of its vigorous polemic.

Chemists, too, will notice with interest the recurrence in essay after essay of one theme in particular—that of the orientated, elastic, thread-like protein molecule. One might, to change the metaphor, venture to call the book a biochemical rosary threaded on this protoplasmic string.

Taking it all in all, this is one of the most fascinating and satisfying volumes encountered for many months, and this fact must be allowed to mitigate, if not to justify, the reviewer's prolixity. The book in some places is as exciting as a good detective story and in others has the romance of an historical novel; it is difficult to see how it could have been made worthier of its great dedicatee.

A. L. BACHARACH



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