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THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

Deaths

WITH deep regret we record the deaths of the following members of the Society:

Leonard Kidgell Boseley, on January 13th (elected 1898).
W. Heber Green (elected 1909).

The Stability of Vitamin *A* in Cod-Liver Oil Emulsions

BY H. N. GRIFFITHS, B.SC., T. P. HILDITCH, D.SC., F.I.C., AND
J. RAE, M.P.S.

(*Read at the Meeting, December* 7, 1932)

THE use of gum acacia as emulsifying agent in the preparation of cod-liver oil emulsions, and also the "homogenisation" process employed, are factors which might conceivably affect by oxidation the vitamin *A* present in the oil, on account respectively of peroxidase present in the gum acacia and of exposure of a considerable surface of the oil to air during homogenisation. It was thought desirable, since information does not appear to have been published on this point, to carry out a few comparative tests by means of the usual colour reaction with antimony trichloride in chloroform.

A sample of cod-liver oil was emulsified on the one hand with gum acacia, and on the other with gum tragacanth (in which no peroxidase is present): the various emulsions, in all of which chloroform (one part in 400) was present as a preservative, are referred to as follows:

A. Made with gum acacia, and containing 50 per cent. of cod-liver oil—not homogenised.

B. Made with gum acacia, and containing 50 per cent. of cod-liver oil—homogenised.

C. Made with gum acacia (previously heated at 100° C. for one hour to destroy peroxidase), and containing 50 per cent. of cod-liver oil—not homogenised.

D. Made with gum tragacanth, and containing 25 per cent. of cod-liver oil—not homogenised.

E. Made with gum tragacanth, and containing 25 per cent. of cod-liver oil—homogenised.

For estimation of vitamin *A* potency the oils were recovered from the emulsions as follows:

The emulsion (about 10 c.c.) was run into warm water (about 100 c.c.) contained in a separating funnel, and ether (100 c.c.) was added. The mixture was well shaken and allowed to settle. The addition of a small quantity of alcohol caused the mixture to separate into two clear layers. The aqueous layer was run off and extracted twice with a volume of ether similar to that used in the previous extraction. The ethereal solutions were united and washed thoroughly with water until all traces of gummy material had disappeared. After removal of ether and moisture the sample of oil was tested by the method of Drummond and Hilditch (*Empire Marketing Board Report*, No. 35, Technique C, p. 32) for the colorimetric assay of vitamin *A*:

The oil (1 grm.) is accurately weighed out in a volumetric flask (10 c.c. capacity) and dissolved in redistilled chloroform (10 c.c.). Into a glass cell of 1 cm. internal thickness, 0·2 c.c. of the solution is added from a pipette, and exactly 2 c.c. of a 30 per cent. solution of antimony trichloride in chloroform are run in from a burette. During the addition of the reagent the solution is gently shaken, and the blue colour produced is matched in a Rosenheim-Schuster colorimeter. The final match is made at the point of maximum intensity of the blue colour.

For the purpose of this note the values so obtained have been doubled, in order to give results comparable with the Carr–Price figures based upon the employment of 0·2 c.c. of a 20 per cent. solution of the oils in chloroform. The original oil and the emulsions were examined in this way at intervals extending up to 15 months from the date when the emulsions were originally prepared; in the meantime they were stored in well-corked, amber glass bottles kept in a dark cupboard. The results of the colorimetric tests, and also of tests for free acidity in the oils, are given in the appended tables.

	Vitamin *A* test (blue units)					
	Oil	A	B	C	D	E
After 2 days	14·2	13·4	14·0	13·8	14·2	13·6
After 2 weeks	14·2	13·4	14·0	13·8	14·2	13·6
After 6 weeks	14·2	14·2	12·6	14·2	13·0	13·4
After 16 weeks	13·8	13·0	12·2	12·2	12·8	12·8
After 6 months	21·2	11·6	9·6	8·8	12·2	11·0
After 7 months	17·4	12·6	10·4	15·2	14·2	11·2
After 15 months	17·0	9·4	8·4	10·6	10·2	10·2
	Free acidity (as per cent. of oleic acid)					
After 7 months	0·6	1·9	0·9	2·8	0·8	0·9
After 15 months	0·9	3·4	1·9	5·6	2·2	1·5

In addition to the colorimetric tests, the cod-liver oil itself and that from emulsion B (made with gum acacia and homogenised) were very kindly submitted to spectrographic examination for us by Dr. R. A. Morton, at the outset and after storage for seven months, with the following results:

	Extinction coefficient $E^{1\%}_{1\,cm.}$		
		Antimony trichloride test	
	328$m\mu$	572$m\mu$	606$m\mu$
Untreated oil—at outset ..	1·24	1·1–1·15	1·0
Untreated oil—after 7 months ..	1·32	1·31	1·57
Oil from emulsion B—at outset ..	1·25	1·15–1·20	1·35–1·40
Oil from emulsion B—after 7 months ..	1·25	1·23	1·31

Dr. Morton added in his report: "At 328$m\mu$ (*i.e.* at the head of the absorption band attributed to vitamin *A*) the oils were found to be indistinguishable, but B exhibited higher absorption on the ultra-violet side of 328$m\mu$ and also a higher chromogenic value for the 606$m\mu$ band. This might indicate that B had undergone slight oxidative treatment, but its vitamin-*A* potency was unaltered." After seven months, however, the pure oil showed a marked difference in extinction coefficient, whilst B, although giving similar values to those obtained on the first examination, also showed the definite fine structure usually only observed with saponified fats.

The spectrographic examinations thus bear out in these two cases the conclusions derived from the simple colorimetric tests, which may be given in the following terms:

1. For at least four months none of the emulsions showed any appreciable loss in vitamin *A* potency as compared with the original oil. At six months some evidence of change was observable, chiefly in the original oil, where an apparent increase in blue "colour value" was noted, the colour at the same time being much more fugitive than in the earlier tests; a similar erratic apparent increase was noted at seven months in the oils from emulsions A, B, C, and D, but at 15 months it was evident that decline in blue colour values had set in definitely in all cases.

The change in intensity and character of the blue colour from 7 months onwards is more or less common to all the emulsions, and equally to the original oil, and is consistent with the gradual onset of oxidative changes in the oil itself during prolonged storage.

2. So far as the procedure followed in manufacturing emulsions is concerned, the data show that neither constituents (*e.g.* peroxidase) of the agents employed nor exposure to air during the process of "homogenisation" diminish the stability of the vitamin *A* during storage. When, ultimately, depreciation in vitamin-*A* potency set in, the values for the oil itself became erratic at the same time-intervals as those at which the oils from the emulsions began definitely to deteriorate.

3. Cod-liver oil emulsions can be kept for at least four months without appreciable loss of vitamin-*A* potency, and probably for seven or eight months without serious alteration therein, if stored in well-stoppered, amber glass bottles and kept in the dark.

4. The development of free fatty acid in the emulsified oils is interesting, for it was greatest in the non-homogenised emulsion prepared from peroxidase-free gum acacia, and least in the homogenised emulsions from both gums, the value for the non-homogenised emulsion made with ordinary gum acacia also being relatively high. Since it is known that certain anaerobic organisms present in the intestines of marine animals display strong lipoclastic action on marine animal fats, we believe that the explanation of these somewhat anomalous observations may be that the hydrolysis taking place in the emulsions is due to the presence of an organism of this type in minute quantities in the oil employed in the experiments. Conditions favourable to its development appear to exist in the non-homogenised emulsions, but exposure to air during homogenisation destroys the anaerobic organism, and thus indirectly retards the development of hydrolytic rancidity.

We have pleasure in acknowledging the facilities accorded to us by Messrs. Clay & Abraham, Ltd., at whose suggestion the experiments were undertaken.

THE UNIVERSITY,
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DISCUSSION

Dr. F. H. CARR said that the very explicit report of Professor Hilditch gave confirmatory evidence of what was found in most laboratories dealing with cod-liver oil emulsions. He was surprised that no changes had been observed during the first six months; he thought that small, insignificant changes took place from the very beginning. Probably there was a counter-effect due to a change taking place in other constituents of the cod-liver oil, whereby the inhibiting substances which prevent blue colour were gradually disappearing. His own experience had shown that it was possible for a cod-liver oil to show an increase from a blue colour figure of, say, 10 to one of 20. It was probably not true that there was no loss of vitamin *A*.

Mr. N. EVERS, confirming the experience of Dr. Carr, said that he had some Norwegian cod-liver oil which, after being kept in a bottle for 17 years, gave a blue colour value of about double that of the normal present-day Norwegian oils. He did not know what was the vitamin value of this sample. After being kept for a further four years this oil still had a value of 8·8, and, when examined spectrographically, showed a distinct inflection at 328 $m\mu$.

Observations on Changes in Raspberries after Picking

By THEODORE RENDLE

(Read at the Meeting, November 2, 1932)

In all problems associated with fresh fruit due allowance must obviously be made for the influence of life actions, and changes resulting from these actions are among the well-recognised phenomena of fruit-handling; in fact, there is a voluminous literature on the subject. Unfortunately, however, in the very nature of things, apples, pears and citrus fruits have been given prior place; soft fruit, and, to a less degree, stone fruit, have apparently received but scant attention. Further, it is by no means possible to deduce from an example of one fruit the behaviour under given conditions of another, so that the available literature is but little guide to what may be expected with raspberries, for example.

In the course of a long investigation in the Research Laboratories of Messrs. Chivers & Sons, Ltd., on some phases of fruit-handling, involving a great many analyses of soft and stone fruits, certain phenomena associated with raspberries were incidentally noted. I am indebted to Messrs. Chivers' courtesy for permission to publish some account of these, and to the research staff for their co-operation.

It is common knowledge that, of all fruits, raspberries are perhaps the most difficult to keep intact, and to transport or handle other than in a state of semi-mush or pulp, and, judging from comparison with other fruits, their fragile nature is to be associated with the speed with which changes in raspberries take place—a speed far greater than with other fruits, though whether their weak structure is cause or effect is a debatable point.

While, in the main, these changes result from a continuation of life processes from within, the onset from without of organisms, such as yeasts, moulds and other agents, plays its part, and physical damage of the skin and structure of the fruit makes the changes of the second kind more rapid and easy.

The larger proportion of raspberries grown in the British Isles is destined for jam, and, as the actual degree of ripeness for this purpose allows a comparatively wide margin, this aspect has not concerned the grower so much as the cost of picking; hence it is the common practice, under normal conditions, to pick a field of this fruit as seldom as possible consistent with the over-ripe berries not maturing beyond a usable condition—generally about every five days. This has tended to obscure the recognition of the speed of those life actions comprehensively described as "the ripening process," which, in common with other changes in raspberries, is remarkably rapid. The necessity of obtaining, for certain purposes, fruit of a definite degree of ripeness has shown that actually 48 hours is ample time even under average weather conditions in Scotland (the home of the raspberry) for the fruit to change from a decidedly unripe state to one of maturity or ripeness; in fact, the change in the popular "Lloyd George" variety is even more speedy. Moreover, the changes associated with ripening continue even faster after the fruit is actually picked. This was shown when under-ripe raspberries

were carefully picked, handled so as to preserve individual berries undamaged, and kept under observation. They were found definitely to alter in texture, colour and flavour—to ripen—in the course of two or three hours. Thus, fruit picked and graded according to degree of ripeness on the field was found, two hours later in the factory, to need re-grading to conform to the same standards of ripeness.

VOLATILE ORGANIC SUBSTANCES IN RASPBERRIES.—Another aspect of an unsuspected change in the ripening of raspberries is the presence of comparatively large quantities of volatile organic substances in the freshly-picked fruit. Freshly-picked raspberries which showed no evidence whatever of fermentation or other decomposition, and which would be accepted as perfectly sweet by a discriminating consumer, were reported by a Public Analyst as containing, in several samples tested, from 0·33 to over 4 per cent. by volume of alcohol, and a determination, made by the orthodox distillation and specific gravity method with suitable corrections for any volatile acid, confirmed his figures.

Further investigations on other samples of fruit gave similar results, and a series of large-scale distillations of selected freshly-picked fruit was made. For these, 1 cwt. of raspberries, without the addition of water, was taken and distilled in one parcel in a steam-jacketed still. The distillate was collected gallon by gallon, the first three gallons were re-distilled with a column, and the first fractions again re-fractionated. From 1 cwt. of fruit, 15 to 20 c.c. (the equivalent of 235 to 313 parts per million or about 0·03 per cent.) of liquid of constant boiling-point 77° to 78° C. was obtained. The difference between this figure and those already quoted is explained by the fact that, in the first case, the fruit had been stored for some little while in a frozen state, whereas, in the second instance, the fruit was distilled immediately after picking. Opportunity was lacking to investigate fully this liquid, but, if it was not wholly ethyl alcohol, it certainly contained a considerable proportion of this body.

A small quantity of lower-boiling fractions was also obtained, and a more careful further fractionation might have shown an even larger quantity of these volatile bodies to be present than is given above. The tests were repeated, and the results confirmed; in fact, it has not been found possible to obtain raspberries entirely free from alcohol-like bodies, even when picked slightly under-ripe direct into vessels containing boric acid to prevent any possible change due to microbiological action after picking.

For comparative purposes, strawberries, black currants, and damsons were distilled under the same conditions, but only a trace of volatile bodies could be separated, even when the picked ripe fruit was kept for some time before distillation.

I have not been able to find in the literature any record of volatile matter in ripe raspberries to shed light on the phenomenon, and it would seem either that raspberries differ markedly from other fruits in the amount and character of their volatile constituents, or, what I believe is more probable, that they are susceptible to far more rapid changes during the ripening and post-ripening stages than is usually supposed. Perhaps it may be said that the character and degree of enzymic activity in raspberries are considerably more marked than in other fruits.

EFFECT OF CHANGES ON THE PECTIN IN RASPBERRIES.—That this rapid change is also reflected in the character of the pectin present in raspberries is shown by a

series of experiments in which these changes were observed through variations in the "gelling" property of the fruit when kept for shorter or longer periods under controlled conditions.

The pectic bodies of fruit have been divided into protopectin, pectin and pectic acid, and methods have been suggested for the determination of each of these substances separately. Moreover, it is stated that the first and last-named do not form jellies with sugar and acid, and that pectin does. While, in the main, this may be true, and such analytical data as may be given by these tests may well provide a basis for the deduction of facts in the hands of an expert familiar with the subject, I suggest that it is doubtful if even such a rough classification exists in nature, and the gradation from one extreme to the other probably covers an infinite number of modifications of the first-formed pectic body.

For these reasons the actual "gelling" property of the fruit under standardised conditions was chosen as the index of pectic changes, but, at the same time, the pectin and total pectic-content was determined by the Carré and Haynes method. In these experiments an extract was made by boiling 3½ lbs. of the fruit with 14 ozs. of water for 15 minutes, and the extract was separated from the pulp and seeds by pressing in a screw hand-press through a fine cloth, the same conditions of pressing being observed in each experiment.

Of this extract, 1½ lbs. were boiled with 18 ozs. of refined crystal sucrose down to a final total weight of 27 ozs., which gives 66·6 per cent. of added sugar in the final product. The hot jelly was filled out, allowed to cool, and stand for 24 hours. It was then tested for jelly strength in the B.A.R.* jelly-tester. Essentially this instrument gives an index of the strength of the jelly under examination in terms of the weight required to revolve through 30° a metal spade of standard dimensions inserted in the centre of the jelly, which jelly is contained in a vessel of standard size and shape. Experience with this tester has shown that concordant and reliable figures can be obtained, provided that the strength of the jelly under test is kept within certain limits. Under these conditions a jelly-strength figure of 25–30 would represent a stiff gel, whereas a strength of from 12–14 would be on the border-line of jelly formation, and certainly any material giving a figure below 10 could not be described as a jelly at all. I am aware that a formula has been published for use with the instrument, which gives values described as "rigidity." This formula has not been used for the figures given in the present paper.

For the Carré and Haynes method 25 c.c. of the extract were employed, and the pectin was precipitated as calcium pectate. The acidity of the extract was determined by the titration of 25 c.c. with N sodium hydroxide solution, and, for convenience, was returned in terms of citric acid. The figures given for total pectin were obtained by determining the pectin as calcium pectate in an aliquot portion of an extract of 2 litres containing the combined extracts from 50 grms. of the original fruit boiled for three successive three-hour periods with $N/75$ hydrochloric acid.

For the study of the pectic changes occurring in raspberries, freshly-picked fruit, almost but not quite fully ripe, was selected, and handled so that the berries

* British Association of Research for the Cocoa, Chocolate, Sugar Confectionery and Jam Trades.

suffered the minimum of physical damage. Control tests were made immediately, and similar tests were made again with the same fruit after it had been held for 24 hours at room temperature (65–75° F.). Further similar tests were made on the fruit after the lapse of six days. The results are given in Table I.

TABLE I

FRESH RASPBERRIES STORED AT 65–75° F.

Storage, No. of days	Extract: Acidity as citric Per Cent.	Extract: Pectin Per Cent.	Extract: Jelly strength	Extract: Jelly	Total pectic-content Per Cent.
0	1·36	0·54	22·0	Firm	0·92
1	1·36	0·45	10·1	None	—
6	1·46	0·17	—	None	0·34

It will be at once apparent that the gelling power of the fruit, which when freshly picked was quite good, very materially dropped in the first 24 hours, and at the end of the test period had fallen so far that it was not capable of forming a jelly at all.

From a large number of further experiments made, the examples given in Table II were selected.

TABLE II

FRESH RASPBERRIES STORED AT DIFFERENT TEMPERATURES

Temperature of storage °F.	Hours in store	Extract: Acid as citric Per Cent.	Extract: Pectin Per Cent.	Extract: Jelly strength	Extract: Jelly	Extract: p_H	Total pectic-content Per Cent.
65–75	0	2·07	0·41	16·5	Rather weak	3·07	0·72
92–99	24	2·02	0·34	11·6	None	2·99	0·68
92–99	48	1·97	0·33	8·0	None	3·04	0·65
65–75	24	2·00	0·40	11·0	None	3·06	0·66
65–75	48	2·00	0·39	10·7	None	3·05	0·66
33–34	24	1·95	0·36	13·8	Very weak	3·00	0·62
11–19	24	2·00	0·44	15·7	Rather weak	3·00	0·65

For these tests fruit similar to that in Table I was employed, but the temperature, as well as the time of storage, was varied. In this series of tests the figures for acidity, percentage of pectin in the extract, and the percentage of total pectin in the fruit show comparatively little variation throughout, but the character of the pectin as reflected in its power to form pectin-acid-sugar gels varies very considerably. The results show very definitely that the variation is associated with the two factors of temperature and time, and that even storage for 24 hours well below freezing-point results in slight damage to the jelly-forming character of the original pectin. It may be added that precautions were taken to adjust the fruit to the storage temperature in the course of an hour.

That such a change should take place, and that it is conditioned by the time and temperature factors, is neither new nor surprising, but the speed with which this change takes place is a point plainly shown by these experiments, and one to which I wish to call special attention. Indeed, as Table II shows, the pectin in

freshly-picked ripe raspberries so changes in 24 hours' storage at normal summer room temperature that their power to form a sugar-acid-gel disappears completely. It may well be that failure to recognise this is responsible for the divergence of opinion which has often been expressed concerning the ability of raspberries to produce a jam of firm consistence without the addition of pectin from other sources, and it is evident that the very rapid character of the natural changes occurring in the pectic bodies in raspberries makes it extremely difficult in large-scale working to produce jam sufficiently firm without the use of added pectin.

A further series of experiments was conducted in which the fruit was, on the one hand, stored between 10 and 15° F. for some months, and, on the other hand, was similarly stored after first having been raised to a temperature of 180° F. to arrest biological changes. In the first case the gelling power of the pectin completely disappeared in about six months, though no appreciable decrease in pectic-content or acidity was shown by analysis; whereas in the second case the full gelling power of the original pectin was retained for at least a year.

CHANGES IN BLACK CURRANTS.—For purposes of comparison, black currants were similarly studied; and, while changes of the same order were noted, they were decidedly less marked, and there was evidence with fresh ripe fruit that only after 8 months' storage at 10–15° F. was there any noticeable decrease in the gelling power of the pectin originally present, and that even then such decrease was quite slight.

EFFECT OF CHANGES ON ADDED PECTIN.—This striking difference between the behaviour of raspberries and other fruits in regard to pectic changes is further demonstrated when pectin from other sources is mixed with the fruit and stored. Purified apple pectin, and also citrus pectin, in aqueous solution, were mixed, respectively, with raspberries and black currants in such proportion that an extract of the mixture when boiled with sugar to 66·6 per cent. sugar concentration gave a stiff gel. Controls with the fruit alone and with the solution of the pectin alone were similarly treated. Gels were made at the commencement of the experiment, and after 24 hours' storage at 95° F., both with and without prior heating to 180° F. to arrest biological change. The acidity was adjusted to a common standard throughout. The results are given in Table III:

TABLE III

CHARACTER OF JELLIES WITH RASPBERRIES AND BLACK CURRANTS PLUS ADDED PECTIN

Fruit	Storage	Fruit alone	Apple pectin alone	Citrus pectin alone	Fruit plus apple pectin	Fruit plus citrus pectin
Raspberry	Fresh	Soft	Firm	Firm	Firm	Firm
Not heated	24 hrs. at 95° F.	Pract. none	Firm	Firm	Soft	Soft
Black currant	Fresh	Firm	Firm	Firm	Firm	Firm
Not heated	24 hrs. at 95° F.	Less firm	Firm	Firm	Less firm	Less firm
Raspberry	Fresh	Soft	Firm	Firm	Firm	Firm
Heated	24 hrs. at 95° F.	Soft	Firm	Firm	Firm	Firm
Black currant	Fresh	Firm	Firm	Firm	Firm	Firm
Heated	24 hrs. at 95° F.	Firm	Firm	Firm	Firm	Firm

There was no need in these cases to measure the strength of the gels—the differences were too marked—for in every case where raspberries were kept in contact with pectin, its gelling power was practically destroyed in 24 hours, whereas this pectin alone or in contact with another fruit, such as black currants, suffered little loss in strength.

To meet the suggestion that, owing to the difference in structure of raspberries and black currants, the pectic substances of the former are more amenable to attack, a parallel series of tests was made with whole black currants and with similar fruit first minced. The results were identical within the limits of experimental error.

In a general survey of the literature on changes taking place in the ripening and post-ripening stages of apples and similar fruits (which changes extend over comparatively long periods), the impression is gained that, in the main, the pectic substances vary somewhat as follows:

(i) in very unripe fruit: mainly protopectin and a little soluble pectin are present,

(ii) in ripening fruit: a considerable increase of soluble pectin, with comparatively little decrease of protopectin, is found,

(iii) in the later stages of ripeness: general degradation of pectic substances, concurrent with the general softening of the fruit structure, occurs.

These changes are ascribed to hydrolysis by the joint action of fruit acids and enzymes.

Changes in raspberries are far too rapid to study in this way step by step, but it is evident, from the experiments above given, that the fruit acid plays little, if any, part in the degradation of the pectic substances, for when fruit containing the full quantity of natural acid, but in which enzymic action has been arrested by heat, is stored, little, if any, change of the pectic substances takes place. On the other hand, it would seem that not only are the changes to be attributed almost entirely to pectic enzymes, but the quantity or activity of these enzymes in raspberries is higher than is generally supposed.

To summarise: (1) The ripening process in raspberries is more rapid than in most fruits.

(2) Accompanying the ripening of raspberries there occurs the production of a comparatively large amount of volatile organic substances not due to the action of micro-organisms.

(3) The pectic substances of raspberries are subject to rapid change, with the destruction of their gelling power; this change is arrested by the application of heat.

(4) It is suggested that the enzymic activity of raspberries is greater than in most British fruits, and is responsible for the above phenomena.

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Discussion

The President was sure that this interesting paper would throw light on a very difficult problem. It had often been alleged that good raspberries were not grown in Kent, and he, personally, had often been asked by jam manufacturers if he could not find a raspberry which would produce a good jam. Mr. Rendle had given an explanation of changes that occurred, including one of which no one was aware until Mr. Rendle had discovered it. The "Lloyd George" raspberry was extensively grown because, he thought, it was very resistant to the attack of parasites, and he was very pleased to know that the fruit was no worse in this respect than other varieties. He had often wondered why, with raspberries, one only liked them very fresh, and the fact that alcohol was rapidly produced probably explained this.

Dr. Buston thought that the results of the work were somewhat surprising. He agreed with Mr. Rendle that, so far, very little had been done on pectin in soft fruits. He asked whether the alcohol which Mr. Rendle had obtained to the extent of 4 per cent. was ethyl alcohol. Was there no methyl alcohol present? One knew that pectin rapidly underwent demethylation, and demethylation was generally associated with loss of jelling power. In the first table (1 to 6 days) the pectin dropped from 0·9 to 0·3, and the soluble pectin from 0·5 to 0·17. He noticed that there was a missing figure on the second day. Had Mr. Rendle any information about the intermediate days? Very probably there were two enzymes at work, one of which simply removed the methyl groups, whilst the other completed the breaking up. Did they act side by side or did the demethylating enzyme act first? A more complete record of "total pectin" and "jelly strength" over the 6 days might give further evidence on this point. The other fruits mentioned (damsons, black-currants, etc.) did not seem, at first sight, to be very like raspberries. Had Mr. Rendle any information concerning such fruits as blackberries or loganberries? In his own experience, loganberries ripened very quickly. On one day the bush would bear nice red berries and the next they would be all black and shrivelled, and it rather looked as though rapid action took place in the case of these crossed raspberries. He believed the "Lloyd George" raspberry was popular because it managed to produce two crops in one season. He wondered whether the continual crops were due to the presence of a particularly active or concentrated enzyme which accelerated the ripening process while the temperature lasted.

Mr. W. Partridge pointed out that boric acid, which the author had attempted to use as a means of stopping fermentation, was a very selective preservative, and he did not think it would stop many forms of fermentation. He was rather surprised that the author had not selected salicylic acid, which was an effective means of preventing the production of alcohol. For this reason he could not regard this experiment as finished.

Mr. G. L. Grinling said he felt sure that the author's work would be of great help in canning. The difficulties experienced in getting the fresh fruit canned were enormous ; two hours after picking one was at one's wit's end to know what to do with the fruit.

Mr. C. E. Sage asked if the author had given any consideration to the presence of amino-acids in the fruit, and their action on the sugars and pectin present. Investigations made by Maillard in 1916, and published in *Annalen der Chemie* for that year, showed that reactions took place between the amino-acids and reducing sugars, and that carbon dioxide was one of the products formed. His own experience with raspberries was that when the fruit was canned it lost its value for jam-making, and that after some months such fruit pulp would not form a jelly with sugar alone. A similar loss of pectin occurred with over-ripe apricots,

and in such a condition the pulp would not set to a firm consistence when made into jam.

Mr. R. L. COLLETT questioned whether there was not rather a tendency to attribute to enzymes things which could not be explained in any other way. He would like Mr. Rendle to see whether he could actually isolate an enzyme from the juice of the raspberry, and then to try the effect of this enzyme on pectin substances. He thought it might be interesting to have rather more points plotted on the curve.

Mr. E. B. HUGHES remarked that they had found Mr. Rendle's experience borne out in their factory. For example, canned raspberries, because they had been sufficiently heated, could be kept for a long period without losing jell strength, but when raspberries were treated with sulphur dioxide without heat there was an immediate, rather small drop in jell-strength, and the raspberries then slowly lost their strength. For example:

Sulphited raspberries, not heated before adding SO_2.

		p_H
Pectin in fresh raspberries ..	0·63 per cent.	3·15
After adding SO_2	0·60 ,, ,,	
After 4 months	0·50 ,, ,,	
After 9 months	0·42 ,, ,,	

Canned Raspberries.

Pectin in fresh raspberries ..	0·65 per cent.	3·3
After 6 months	0·64 ,, ,,	

The fall in jell-strength of sulphited raspberries was even greater than the fall in pectin.

Mr. A. MORE thought that alcohol might develop very rapidly owing to the softness of the raspberry. They had found that fresh apple juice contained a small amount, and had wondered whether it was due to fermentation of juice exposed to yeast at the bruises on some apples. Long Ashton Research Station had, therefore, squeezed whole apples for them so that there was no possibility of outside contamination, but the juice was found to contain some alcohol. Regarding the question whether the alcohol found in raspberries contained methyl alcohol, he would say that they had examined cider and found it to contain traces of methyl alcohol.

Mr. T. RENDLE, replying to Dr. Buston, said there might have been a little, but only a little, methyl alcohol present. As was stated in the paper, the volatile liquids obtained were not fully investigated. With regard to the suggestion that alcohol formation was associated with pectic changes, he could not speak very definitely on that point, but some evidence had been obtained that the change in setting power of pectin was not connected with alcohol formation. As regards Table I, he was sorry he had no information about the intermediate steps, neither had he any information about the behaviour of blackberries and loganberries under similar conditions. Mr. Partridge had criticised the use of boric acid, but this was chosen as, in the author's opinion, being less open to criticism than most other preservatives, and, in any case, it was used in the proportion of 1 per cent. on the fruit, and the fruit was distilled very quickly after picking; possible fermentation by yeast was, therefore, in his opinion, adequately safeguarded. He could offer no opinion on Mr. Sage's suggestions about amino bodies, as the subject had not been studied exhaustively—in fact, only the fringe of it had been touched. In his experience, apricots, in almost every instance, contained pectin capable of producing a very excellent jell. Further study of the enzyme action,

as mentioned by Mr. Collett, would no doubt produce results of interest. He was in agreement with Mr. Hughes, that the percentage of pectin decreased when fruit was preserved with sulphite, but he believed that the jelling power decreased more rapidly than did the actual percentage of pectin.

Notes on the Spontaneous Combustion or Ignition of Hay

By F. ROBERTSON DODD, F.I.C.

(*Read at the Meeting of the North of England Section, October* 15, 1932)

As the question whether a stack fire is due to spontaneous combustion or to incendiarism or accidental firing is frequently referred to consulting chemists by insurance companies and others, some help in answering the question may be found from records and notes which I have kept, the following being the salient points:

Hay which fires spontaneously has a smell peculiarly its own, somewhat like that of tobacco. The expert surveyor of stack fires can recognise a probable case of spontaneous combustion almost unerringly by the smell alone, but his company frequently requires scientific confirmation of his opinion to convince the claimant that it is justified in refusing to part with its money.

By the terms of its policy an insurance company is not responsible for a stack, unless incendiarism or accident be proved, for a certain time after its completion; thus spontaneous combustion is never covered by insurance. Hence claims are always based on incendiarism or accidental firing, and, to rebut such claims, the company requires proof that the fire is due to spontaneous combustion. If spontaneous combustion be alleged, it is desirable to know the date of stacking. A stack fires spontaneously between 5 and 13 weeks after it is built—generally between 8 and 9 weeks. The period between stacking and firing is therefore an important point. If the stack has been cut into, the time of its firing is shortened. Badly-made hay, stacked while wet, will heat and fire, and hence many of the claims analysts are asked to examine occur in wet seasons. Yet it is a well-known saying among agriculturalists that "More hay is spoiled in a good season than in a bad one," *i.e.* by heating. In haymaking, during very hot weather, the outside of each grass

stalk becomes dry, while the pith or inside may remain moist: hence the saying. Sunlight is supposed to kill the bulk of the bacilli on the hay, but it is common knowledge that *B. subtilis* and other organisms are readily grown from specimens of hay.

It has been held that these "outside" organisms (thermophilic bacteria, etc.) are responsible for the fermentation leading to spontaneous combustion, but I should hesitate to say that, because I found certain bacteria present, the fire was due to that cause. As a broad rule, it is held that the wetting of hay by rain does not cause spontaneous combustion; it does cause the hay to become mouldy. It is also a generally accepted statement that second-crop hay never fires spontaneously. The question therefore of spontaneous combustion generally arises in September.

Insurance companies instruct their agents that "so long as water-vapour alone is seen to escape from a stack, all may be well, but if a bluish vapour with a sulphurous smell is observed, the stack will certainly fire, unless cut into or the centre cut be away. The safer plan is to spread it abroad until perfectly dry and re-build the stack."* They do not define what is a bluish vapour or what a sulphurous smell, and one is tempted to wonder whether at the back of their minds is the idea that certain sulphur bacteria are the responsible agents.

The evidence from a bacteriological examination of a sample is too questionable to be of much value, and I am inclined to agree with Conn (*Agricultural Bacteriology*, p. 314†) that "it is much more probable that the phenomenon here involved is one of the chemical fermentations due, either to respiratory changes, or to enzyme-like bodies, which bacteriologists are now learning play such an important part in fermentations hitherto attributed to bacteria." That certain changes occur in improperly cured hay when tightly packed in a stack, and that these changes may give rise to spontaneous combustion, we agree. As to the nature of the changes, there is a difference of opinion which will continue until a proper scientific investigation is made.

A confrère (E. G.) holds that methane is produced during the heating of the stack, and that this is the primary cause of the firing. This is an attractive theory in some ways, but I am more inclined to accept the theory of my late partner (Mr. Alfred Smetham), that the enzymes attack the phosphates or phosphatides or both present in the hay (0·5 per cent. P_2O_5), and that phosphuretted hydrogen is the responsible agent.

Whatever the gas, it appears to be held by the watery envelope formed in the tightly-packed hay until, as this gradually dissipates, it finds its way to the outer edge of the stack, when it at once ignites and sets fire to the outside of the stack. Those who have seen stacks firing may recall instances where, on pulling a handful of hay from the interior and throwing it into the air, it has at once burst into flames. I have even had a carefully taken sample which, on removal from the sample bottle, behaved similarly in the laboratory, but such cases are rare.

It is always desirable to know the circumstances connected with any fire

* Harris, *Technological Dictionary of Insurance Chemistry*, published at the Phœnix Fire Office, Exchange, Liverpool, 1899.

† Published by Rebman Ltd., 1901.

and thus get helpful "pointers." For example, an actual case occurred during one of those phenomenally wet summers which we occasionally experience, where a stack 1¼ miles from the River Dee took fire. It was alleged that two enthusiastic fishermen, who were trout fishing in the Dee, ran for shelter to this stack at the onset of a squall, and, while there, spent their time smoking cigarettes and throwing their matches into the stack. They had been out in the rain all the morning, and so I doubted the story. Our tests exonerated them and disproved the statement, which, plausible though it was, might have been used to influence a jury had there been no other evidence.

The tests were made on the hay as it was received, no attempt being made to dry the sample before testing, as volatile acids would be thereby lost, or to calculate the results upon the dry substance, or to the average moisture-content of hay, since the moisture due to the use of a fire hose cannot be distinguished from moisture normal to the heated hay. The hay was cut into small pieces by scissors and the loss at 100° C. was determined in a water-oven.

A weighed quantity was extracted in a Soxhlet tube with ether, the ethereal extract was dried and weighed, and the acidity of the residue was determined by dissolving the dried extract in alcohol and titrating in the usual way.

Another weighed quantity was soaked in neutral alcohol at 70° C., *e.g.* on the top of a water-oven, for exactly an hour, with frequent stirring, and titrated for total acidity without removing the hay.

Typical figures thus obtained during the last 25 years were as follows:

		Loss at 100° C.	Ethereal extract Per Cent.	Total acidity (as lactic acid) Per Cent.	Non-volatile acidity (as lactic acid) Per Cent.	Remarks
1.	Good hay ..	undetermined	0·90	0·39	0·13	6 weeks in stack, N. Wales
2*a*.	Rye grass hay	,,	1·27	0·71	0·26	,, ,,
2*b*.	,, ,, ,,	14·20	1·93	0·85	0·38	13 months in stack, Lancs.
3.	Sound hay ..	13·05	1·37	0·98	0·07	
4.	Heated hay ..	11·95	4·10	2·96	0·83	Spontaneous ignition
5.	,, ,, ..	10·15	4·17	2·89	1·09	,, ,,
6.	,, ,, ..	12·40	4·63	4·18	2·06	,, ,,
7.	,, ,, ..	20·05	3·40	3·09	1·22	,, ,,
8.	,, ,, ..	12·25	3·63	2·51	1·29	,, ,,
9.	,, ,, ..	13·65	4·30	3·60	0·90	,, ,, (8 weeks)
10.	,, ,, ..	26·20	3·40	1·74	1·54	,, ,,
11.	,, ,, ..	15·05	4·23	2·19	1·41	,, ,,
12.	,, ,, ..	13·10	4·53	2·38	1·61	,, ,,
13.	,, ,, ..	9·95	4·10	6·11	1·67	,, ,,
14.	Hay alleged to be heated ..	61·10	1·43	0·60	0·20	Not spontaneous ignition
15.	Heated hay ..	24·90	3·00	3·73	0·84	Spontaneous ignition
16.	Ditto, taken day before fire	13·80	1·37	2·57	0·06	,, ,,
17.	Rye grass hay (2*b*) fired and extinguished	32·90	0·50	0·68	0·19	Experimental

No. 17 was the result of a laboratory experiment on hay, No. 2*b*, the bundle of hay having been heated in an oven until it fired (390° F.), and the fire then extinguished with water.

Nos. 1 and 2 were hays of good quality which had been stacked only six weeks.

Nos. 2 and 2*b* show how slight is the change, if any, in hay after it has reached its equilibrium in the stack.

No. 3, while not of so good a quality as No. 1, represents what may be regarded as an average marketable meadow hay.

Nos. 3 and 4 were from the same stack yard.

No. 9 had been eight weeks in the stack when firing occurred.

No. 14 was mouldy and should not have been referred for examination.

Nos. 15 and 16 were from the same stack on successive days, No. 16 having been taken from one end of the stack and placed in the horses' rack on the day before the fire.

In respect of Nos. 10, 11 and 12, there was not the slightest doubt in the mind of either surveyor or farmer's representative that spontaneous combustion had taken place. The samples were referred for scientific confirmation of their opinions.

Let me add a word of warning that analysts should be watchful lest they be tricked into a wrong admission by the substitution or admixture of ensilage with their sample, that is to say, in cases where they have not inspected the premises where the fire occurred and drawn their own samples.

Some ensilages which I have tested had undergone acetic fermentation to such an extent that the aqueous extract from them contained as much acid as vinegar.

For the guidance of those who are called on to inspect a suspicious stack, *The Farmer and Stockbreeder* for August 8th, 1932, gives the following hints:

Pull out samples with a hay-tester hook. If there is no perceptible heat, the hay will be green. A light brown colour develops at about 120° F.; warm brown colour at about 140°–150° F.; dark brown at about 160° F. Signs of charring appear at about 190° F. At this temperature the stack may be expected to fire. When taking samples to test, find the hottest spot; this will often shift about a stack.

Expert surveyors use a 9-foot spear, in which a thermometer is inserted near the point, and are thus able to take the temperature more accurately.

The wise man turns the hay, or keeps very close watch on it after 150° F. is reached; it not only saves the rick, but saves the feeding value, which is expended as fuel to raise the temperature.

Discussion

Mr. Stock said that he had had experience in only one instance, and in that case the analytical figures, when compared with those communicated to him by the author, were such as to show that the fire was due to spontaneous ignition; there seemed to be no literature on the subject, and, consequently, the whole question appeared to be one eminently suitable for examination under the Society's Analytical Investigation Scheme, particularly with a view to some research into the character of the acid bodies produced by the processes of fermentation taking place in a heating stack.

Effect of Heat-Treatment of the Metal on the Determination of Silicon in Aluminium, and the Loss of Volatile Silicon Compounds in the Mixed Acid Method of Solution of the Metal

By L. H. CALLENDAR, Ph.D., F.I.C., A.R.C.S.

In a previous paper (Analyst, 1932, **57**, 500) experimental details were given of the following four methods most commonly used for the determination of silicon in aluminium:

(*a*) Mixed acid process, in which the metal is dissolved in a mixture of sulphuric, nitric and hydrochloric acids.

(*b*) Sulphuric acid method (solution in sulphuric acid of sp.gr. 1·6).

(*c*) Soda method. The metal is dissolved in 10 per cent. sodium hydroxide solution in a nickel crucible, the solution is boiled to convert silicon into silica, and then poured into excess of sulphuric acid.

(*d*) Sulpho-nitric acid method (solution in concentrated nitric acid *plus* 60 per cent. sulphuric acid).

A comparison of the results given by these four methods with the same set of samples of aluminium, of various silicon-content, but all annealed at 550° C. for 24 hours and then quenched in cold water, showed differences of as much as 20 per cent. between the methods.

Table I

Comparison of Silicon Analysis Methods

Metal	Iron Per Cent.	Silicon, per cent. Soda method	Mixed acids	Sulpho-nitric	Sulphuric acid
E.	0·30	0·18	0·14	0·17	0·14
K.	0·33	0·23	0·20	0·22	0·19
V.	0·31	0·34	0·28	0·33	0·29
R.	0·32	0·40	0·38	0·42	0·33
C8.	0·32	0·69	0·57	0·69	0·52
C10.	0·46	1·32	1·15	1·32	1·14

Note.—The silicon figures are the mean of duplicate determinations on 5 grms. of metal (except C10, of which only 2 grms. were used). The order of agreement between duplicates in these experiments was ± 0·005 per cent. of silicon.

It will be seen that the soda and the sulpho-nitric acid processes agree well, and that there is also fair agreement between the results by the mixed acid and sulphuric acid processes; the results given by the latter two methods, however,

are about 20 per cent. lower than the results with the former two methods. After elimination of errors common to all methods of silicon analysis, as discussed in the previous paper, there seems no reason to suppose that the results by the soda method can be too high, since the results of parallel blank experiments with the chemicals gave less than 0·0001 grm. of silica. The conclusion must be drawn that the mixed acid and sulphuric acid processes give low results with this class of metal, and, since other likely sources of error have previously been considered, and means have been taken to eliminate them, it follows that this loss takes place during the solution of the metal.

With aluminium metal containing silicon, heat-treatment at 550° C., followed by quenching, tends to leave the silicon in solid solution (up to about 1·5 per cent. of silicon), *i.e.* the silicon is in the finest possible state of division. If, however, the metal is heat-treated at 300° C. and quenched, a part of the silicon may be precipitated in a sufficiently coarse state to be visible under the microscope. It was thought that metal, heat-treated in the latter manner, might show less loss of silicon during solution in acid, and the results in Table II for the same metal as in Table I show less loss by the mixed acid process after the metal has been annealed at this lower temperature.

TABLE II

EFFECT OF HEAT-TREATMENT OF METAL ON MIXED ACID RESULTS

Sample	Mixed acid process		Soda method (Any annealing procedure) Silicon Per Cent.
	Annealed at 550° C. and quenched Silicon Per Cent.	Annealed at 300° C. and quenched Silicon Per Cent.	
E.	0·14	0·17	0·18
K.	0·20	0·22	0·23
V.	0·28	0·33	0·34
R.	0·38	0·37	0·40
C8.	0·57	0·61	0·69

The variations of the silicon figures with heat-treatment of the aluminium, shown in Table II, are clearly very important to metallurgists, as the possibility of such variations tends to throw doubt on the accuracy of all investigations in which the mixed acid process has been used for the determination of total silicon in the metal, *i.e.* of nearly all the investigations on aluminium published during the last forty years in which figures for silicon in the metal have been given. I have been fortunate, therefore, to obtain some entirely independent confirmatory results obtained with different metal by different analysts. The results of these confirmatory experiments, in which the soda, mixed acid, and hydrochloric acid methods of solution are compared, are given in Table III.

Since it appeared that the loss of silicon must occur during the solution of the aluminium metal in acid, it was decided to carry out some experiments to see whether silicon could be detected in the gases evolved during the actual solution of the metal in mixed acids.

TABLE III

CONFIRMATORY RESULTS SHOWING EFFECT OF HEAT-TREATMENT OF THE METAL ON THE FIGURES OF THE SILICON DETERMINATION

Sample		Method	Temperature of annealing: 300° C. Silicon, per cent.	Temperature of annealing: 550° C. Silicon, per cent.
A.	(Fe=0·31 per cent.)	Soda	0·58	0·58
		Mixed acid	0·56	0·46
		Hydrochloric acid only ..	0·49	0·23
B.	(Fe=0·35 „ „)	Soda	2·04	2·03
		Mixed acid	2·07	1·70
		Hydrochloric acid only ..	2·05	1·25
C.	(Fe=0·60 „ „)	Soda	0·28	0·28
		Mixed acid	0·27	0·25
		Hydrochloric acid only ..	0·22	0·12

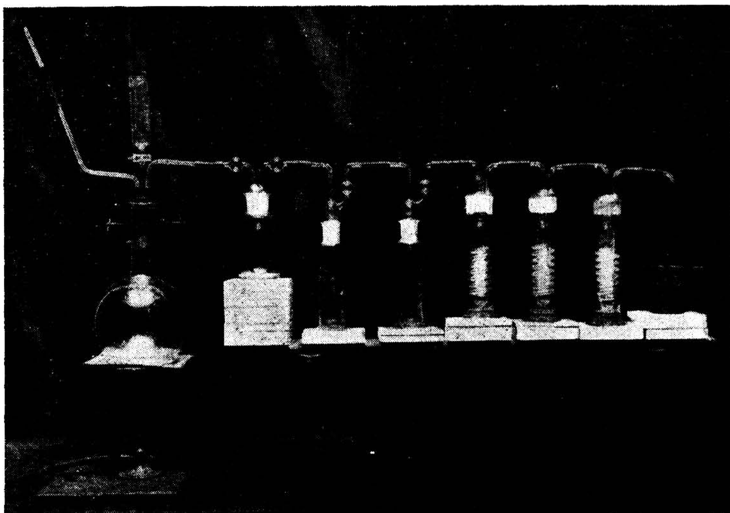
DETECTION AND DETERMINATION OF VOLATILE SILICON COMPOUNDS.—As long ago as 1857 Wöhler and Buff stated that silicon hydrides were evolved when aluminium was acted on by hydrochloric acid. In 1868 Rammelsberg (*Ber.*, 1868, **1**, 222) prepared an aluminium-silicon alloy, and found that when this was treated with hydrochloric acid the free silicon in the alloy remained behind as a black residue, but the combined silicon was partly converted into silica, and partly lost as silicon hydride. In 1891 Regelsberger (*Z. angew. Chem.*, 1891, 442) suggested that the gases evolved from a mixed acid attack on aluminium could be tested for silicon hydrides by passing them through a solution of caustic potash; later work has shown that this method is not satisfactory even as a qualitative test, as the rate of reaction is too slow, *e.g.* it takes 24 hours for a 10 per cent. potash solution to absorb completely the silicon hydrides in such a gaseous mixture. In 1896 Otis-Handy (*J. Amer. Chem. Soc.*, 1896, **18**, 766), of the Aluminium Company of America, probably basing his remarks on Regelsberger's statement, said that the method of mixed acid attack gave oxidising conditions during solution, and so prevented loss of combined silicon as hydride. However, as no experimental evidence whatever was provided to substantiate this statement, little weight can be attached to it.

In 1910 Seligman and Willott (*J. Inst. Metals*, 1910, No. 1, 138) published some results for actual determination of the volatile silicon compounds (which they called SiH_4) evolved from acid attack on aluminium, but, probably owing to unsatisfactory absorption, their results appear to be much too low.

It is evident that investigators in the past were handicapped by an incomplete knowledge of the properties of silicon hydrides, especially in relation to the rate of reaction of these substances with alkalis and oxidising agents, and it was not until the publication of the work of A. Stock and C. Somieski (*Ber.*, 1916, **49**, 111) that there was available any really trustworthy account of the mode of formation and properties of the silicon hydrides.

From Stock's work it appears that in acid attack on magnesium silicide six different silicon hydrides may be formed, and, in addition, a solid silico-oxalic acid is usually formed in considerable amount. My experiments with aluminium have shown that the volatile silicon compounds formed during acid attack on the metal possess certain of the properties of the silicon hydrides described by Stock, and, further, that a white solid body is formed under conditions similar to those described by Besson (*Compt. rend.*, 1912, **154**, 1603); Besson gave his compound the formula $Si_3O_5H_3$—a silico-oxalic acid type.

The following experiments have been limited to a qualitative demonstration of the formation of volatile silicon compounds in acid attack on pure aluminium and aluminium-silicon alloy. No attempt has been made at an exact quantitative determination or identification of these compounds, as this seemed to be too far outside the scope of the main research.



Absorption Apparatus for Silicon Compounds.—It was proposed to absorb the gases given off during the solution of aluminium in various acids, and to determine the amount of silicon found in the liquids used for the absorption. For this purpose, after a number of preliminary trials, the apparatus shown in the figure was used. The chief part of this apparatus is the absorption train. This consists of three spiral gas-washing bottles, the spiral train having a total length of 360 cm.; through this the whole of the gas must pass, bubble by bubble, in contact with the absorbent. The issuing gases are passed (by means of a rubber funnel) into a large nickel crucible containing caustic soda. The 2-litre flask is provided with a tap funnel and a safety tube; through this tube, a current of air could, if required, be admitted into the flask to drive out all the residual gases. The first two wash-bottles contain water, the next contains about 1 c.c. of liquid bromine in bromine water; the succeeding three absorption bottles contain saturated

bromine water. The double nickel crucibles (a small one inside a larger one to prevent splashing) contain 10 per cent. caustic soda solution. The silica was determined in these liquids by "fuming" with excess of sulphuric acid and treating the residues with hydrofluoric acid as usual. It is not maintained that this is an exact quantitative method, but it was sufficiently accurate for the qualitative results required.

The use of bromine water and soda as absorbents was based upon the work of Stock. The silicon hydrides react with bromine, the higher hydrides being the more reactive, to form compounds of the type SiH_3Br, SiH_2Br, $SiBr_4$, etc. These compounds are highly volatile, but most of them are readily decomposed by water; their decomposition is, however, much more rapid and complete when brought about by caustic soda solution.

The experimental results given in Table IV illustrate absorption by the bromine-soda method. For these experiments a metal was used which contained its silicon mainly in the dissolved state. Two grms. of metal were dissolved in 100 c.c. of hydrochloric acid (1:1) in the apparatus described above, and the silica was determined in the flask, in the bromine bottles, and in the soda solution.

TABLE IV

ABSORPTION OF SILICON COMPOUNDS BY BROMINE SODA

Exp.	Metal	Silica in flask Per Cent.	Silica in bromine Per Cent.	Absorbed in soda Per Cent.	Total found Per Cent.	Calculated from soda analysis Per Cent.	Unabsorbed, loss per cent. of total present
346 S.	C.9	0·0426	0·0090	0·0064	0·0580	0·0570	Nil
343 R.	C.10	0·0374	0·0086	0·0008	0·0468	0·0587	20
349 N.	C.8	0·0152	0·0050	0·0058	0·0260	0·0306	15
352 N.	R.2	0·0044	0·0042	0·0054	0·0140	0·0177	21

S = slow rate of solution; R = rapid rate of solution; N = not timed.

These results show that the volatile silicon compounds given off in acid attack can be absorbed, to a greater or less extent, by bromine-soda. The degree of absorption is naturally influenced by the rate at which the gases pass through the absorbents, and in experiment 346, in which the whole of the silicon was recovered, the rate of evolution of gas was kept low by cooling the flask; it should also be noticed that at the end of this experiment a larger proportion of the total silica was found in the reaction flask.

The next experiments show comparable results from soda, mixed acid and sulpho-nitric acid attack on the same metal, in one case with silicon present in the dissolved state, and in another case after annealing at 300° C., with the silicon precipitated from solution in the metal. These experiments show definitely that in mixed acid attack on metal containing dissolved silicon some volatile silicon compounds will be lost from the analysis.

The results given in Table V are very important, as they show definitely a loss of volatile silicon compounds in the mixed acid attack on both pure aluminium and aluminium-silicon alloy; and they further show that the amount of this loss is influenced by the annealing treatment of the metal.

TABLE V

SILICON COMPOUND LOSSES FROM ANNEALED METAL

Exp.	Metal and annealing treatment	Total weight taken Grms.	Weight dissolved each time Grm.	Acid or alkali used c.c.	Absorbed silicon in bromine-soda, less blank (0·0006 grm.) Grm.	Loss of silicon per grm. of metal Grm.
430–1	High silicon alloy A.9 annealed at 550° C.	20	1	35 of mixed acids	0·0122	0·0006
436–7	Pure metal C.9 annealed at 550° C.	10	1	35 of mixed acids	0·0058	0·0006
432–3	High silicon alloy A.9 annealed at 550° C.	10	0·5	20 of 10 per cent. soda	Nil	Nil
438–9	Pure metal C.9 annealed at 550° C.	10	0·5	20 of 10 per cent. soda	Nil	Nil
434–5	C.9 annealed at 550° C.	4	2	100 of sulpho-nitric acid	0·0006	0·00015
444–5	Silicon alloy A.9 annealed at 300° C.	10	1	35 of mixed acids	0·0034	0·00034
440–1	Pure C.9 annealed at 300° C.	10	1	35 of mixed acids	0·0008	Less than 0·0001
442–3	Pure C.9 annealed at 300° C.	10	1	40 of 10 per cent. soda	0·0006	Less than 0·0001

In the soda method of attack it appears as though no volatile silicon compounds were formed, so that the method would appear to be free from this error inherent in the mixed acid process.

SILICO-ACIDS AND SPURTING LOSSES.—Even on the assumption that only some 50 per cent. of the volatile silicon compounds given off during the acid attack on the metal are absorbed in the gas bottles, the amount of silicon found is clearly not equal to a 20 per cent. loss—the difference between the results by the mixed acid and soda methods. Under the ordinary conditions of experiment there must, therefore, be some other source of loss of silicon in the mixed acid process.

During the solution of the metal in hydrochloric acid it was noticed that a white cloud filled the reaction flask and a white powder condensed in the first connecting tube. This white powder was found to contain about 50 per cent. of silicon, and was possibly a silico-oxalic substance, but, as stated previously, it was not identified. This substance was washed back into the flask for the determination of the silicon remaining behind, but it would appear that in an ordinary silicon determination carried out in shallow beakers the greater part of this semi-volatile silico-compound would be lost. Owing to the fact that, in the mixed acid attack, the brown fumes of nitrogen peroxide obscure any other fumes, there is no visual evidence that any similar compound is formed. Nevertheless, without specifying

the nature of the substances lost in this way, it is at least possible to determine the amount of silicon which they contain, by using a somewhat different apparatus in which to carry out the acid attack on the metal.

For this purpose, a large desiccator, fitted on the top with a ground-in tap, was substituted for the reaction flask. The covered shallow beakers containing weighed amounts of metal and the acid to be tested were placed in the desiccator (with mixed acid the beaker and contents were first warmed to start the reaction), the lid put on firmly and the exit tap connected with the absorption train used for previous experiments. When the reaction had practically ceased, the beaker was withdrawn, the outside of it being washed down into the desiccator. Three determinations were made: (i) The silica remaining in the beaker; (ii) the silica found in the desiccator, *i.e.* the spurting and silico-acid loss; and (iii) the silica in the bromine absorption train. Twenty-five such determinations on three classes of metal were carried out by the mixed acid process, and, for comparison, ten determinations with hydrochloric acid and ten by the soda method were made in nickel crucibles. The results of these experiments are given in Table VI.

TABLE VI

SPURTING AND OTHER LOSSES IN SILICON DETERMINATION

Method	Treatment	One-grm. samples taken	Silicon in beakers Per Cent.	Collected from desiccator (Mean) Per Cent.	Gaseous loss (Mean) Per Cent.	Total silicon found (Mean Si) Per Cent.
Mixed acids	*A* as cast (iron=0·32 per cent.)	10	0·46	0·024	0·005	0·49
,, ,,	*B* annealed at 300° C. (iron=0·40 per cent.)	5	1·11	0·013	0·007	1·13
,, ,,	C.9 annealed at 570° C.	10	1·03	0·180	0·055	1·27
Hydrochloric acid only	,, ,, ,,	10	0·69	0·145	0·205	1·04
Soda method	,, ,, ,, 24 hrs. and quenched	10	1·30	0·001	Nil	1·31

Note.—C.9 was another sample from the same casting as C.10 (Table I). All results are corrected for blank determinations on the chemicals.

The results in Table VI tend to show that in a silicon analysis carried out in beakers by means of the mixed acid process there is likely to be some loss of silicon as volatile silicon compounds, and, further, that the amount of this loss appears to vary with the heat-treatment of the metal.

These results also show that when the soda method is used under similar conditions there is no appreciable loss of silicon as volatile silicon compounds.

It appears that these results give the explanation of the differences between the figures of silicon-content obtained by the soda and mixed acid processes on the same samples of metal (Table I), and the conclusion is therefore reached that for the determination of silicon in aluminium and its light alloys the soda method is the most accurate; the sulpho-nitric acid method (from the results in Table I)

is practically as good, but the mixed acid and sulphuric acid processes are liable to give low and variable results, and are therefore unsuitable for analysis where a high order of accuracy is imperative.

The work described in this paper was carried out in the Research Laboratories of the British Aluminium Company at Warrington, and I wish to acknowledge my indebtedness to the Company for permission to publish the paper.

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 REACTION OF HUMAN MILK

SPARSE information is available on the reaction of human milk; most authors of works on physiological chemistry and others who might be expected to deal with the matter do not mention it.

The only references that I have found are the following:—Hammarsten (*Text-Book of Physiological Chemistry*, Seventh Edition, 1914, p. 660), after mentioning that "woman's milk is amphoteric in reaction," quotes Courant as stating that "one hundred c.c. of the milk had the same average alkalinity as 10·8 c.c. of $N/10$ sodium hydroxide solution and the same acidity as 3·6 c.c. of $N/10$ acid."

Sommerville (*Practical Sanitary Science*, Second Ed., 1914, p. 153) says that human milk is almost always alkaline.

H. D. Richmond (ANALYST, 1908, **33**, 114) gives analyses of eight specimens of human milk and includes the following figures for acidity:—5·5°, 2·8°, 3·7°, 3·7°, 3·7°, 4·7°, 9·3°, and 5·5°. These would be the conventional "dairy degree of acidity," *viz.* c.c. of $N/10$ alkali required to neutralise 100 c.c. of the milk, with phenol-phthalein as indicator. I have used this denomination in the table that follows.

With a view to ascertaining first what the limits for acidity were; and secondly, whether the figure was likely to prove useful in one way or another, I have, where possible, determined it on specimens received in the last fourteen years. The small number of these analyses (there are only fifteen) is due to the fact that inadequate amounts are usually received, but, as there is the underlying suggestion that a high acidity is abnormal, others better placed than I for demanding "full feeds" as specimens for analysis may think the matter worth investigation.

The highest acidity found by Richmond (9·3°) being on a milk showing a wide variation from the normal (low proteins, high sugar and low ash) it is placed as No. 1 in the table.

These results confirm the suggestion that, I think, may be read into H. D. Richmond's data: that (slightly widening his range) acidity varies in most cases from 2·0 to 5·5 "dairy" degrees.

The fat figures are given for what they are worth, which is "nothing" in many cases, owing to the unfortunate tendency of nurses to apply the breast-pump first and satisfy the infant after, so that first drawings are sent for analysis. Requests for a portion of a full feed are not usually granted. The physician notes the

comment in a report that the fat is only half of what it ought to be, and the suggestion that only the earlier part of a feed has been submitted, and draws the conclusion (which is correct in most cases) that a full feed would show adequate fat.

Serial number	Fat Per Cent.	Proteins Per Cent.	Lactose Per Cent.	Ash Per Cent.	Acidity "Dairy Degrees"	Remarks
1	4·05	0·99	7·03	0·18	9·3	H. D. Richmond's case.
2	3·25	1·74	7·03	0·20	4·2	——
3	2·15	1·48	—	0·21	5·0	Evening specimen.
4	3·33	1·33	6·51	0·23	5·0	Same source as No. 3, but morning specimen.
5	4·0	—	—	0·27	4·0	Premature child (question here was if fat was adequate).
6	2·55	1·89	6·25	0·26	3·5	——
7	1·73	1·61	6·90	0·22	5·5	——
8	1·22	0·52	7·20	0·27	5·0	Food of 4½ months' old baby that was not gaining weight, and had diarrhoea with green stools.
9	1·70	2·00	7·24	0·20	7·5	——
10	3·1	1·26	7·23	0·34	10·0	——
11	1·7	0·8	5·74	0·11	2·5	Food of 3-weeks-old baby not gaining weight.
12	2·1	—	—	0·24	2·7	Mother over 40, anxious to feed child (s.n.f., 8·25 per cent.).
13	2·95	1·30	7·30	0·19	8·2	——
14	3·05	0·60	6·77	0·30	22·0	——
15	5·7	0·60	7·18	0·20	5·0	Baby described by pathologist as having "very undigested stools and some mucus."
16	0·98	2·83	6·17	0·31	4·1	Specimen collected four days after confinement. Colostrum was the predominant constituent.

An editorial in *The Medical Press and Circular* (August 20, 1924) gives the p_H of human milk as 7·1.

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THE EXTRACTIVES OF RUM

IN reference to the note by William Partridge under the above heading in the ANALYST (1932, **57**, 772), it may be of interest to quote some figures obtained about twenty-five years ago by W. Collingwood Williams, and published in the *Journal of the Society of Chemical Industry*, May 31st, 1907.

The twenty-eight samples of rum analysed were received direct from Jamaica at strengths varying from 21° to 44° O.P. They were divided into "common clean" or ordinary drinking rum, and "flavoured" or "German" rum, used solely for blending.

Three of the samples were uncoloured and practically devoid of solid matter; in the remainder the solids varied from 0·14 to 1·16 grms. per 100 c.c., the average being 0·4 for the whole series. If such rums were diluted to the usual strength for sale without any other addition, the solid matters would obviously be about half the above figures. As a matter of fact, fifteen out of the twenty-five coloured samples would contain less than 0·20 grm. of extract per 100 c.c. They would, nevertheless, be properly described as genuine rum.

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THE DETERMINATION OF PHOSPHORUS IN "BASIC" IRON

THE accurate determination of phosphorus in iron and steel has been the subject of much controversy in the past, and many papers have been published dealing with the subject, the most recent being by Etheridge (ANALYST, 1931, **56**, 14). All methods entail the preliminary conversion of the element into the ammonio-phosphomolybdate, in which the phosphorus is determined by titration or by gravimetric methods. The best gravimetric method is the conversion of the "yellow" precipitate into lead molybdate, the method having the advantages of the formation of a stable compound and an extremely low conversion factor of the latter into phosphorus; in addition, the theoretical factor is used ($PbMoO_4$ = 0·7 per cent. P), whereas the phosphorus equivalent of the standard solutions used in the volumetric process is previously found by means of the lead molybdate method or with a steel of known phosphorus content. The gravimetric method, however, is not as rapid as the determination of the phosphorus in the ammonio-phosphomolybdate precipitate by the volumetric method, which is excellent under controlled conditions. The complete separation of phosphorus as ammonio-phosphomolybdate is carried out under definite conditions, and the analysis is straightforward in samples where the phosphorus-content is known approximately, *e.g.* in steels and in irons of low phosphorus-content. It occasionally happens, however, that an analyst receives a batch of irons, the composition of which is not known even approximately, and when it is realised that the phosphorus-content of pig irons varies between 0·05 per cent. and under (in haematite irons) to approximately 4·0 per cent. in some basic pig irons, it is essential to modify the method of analysis to obtain accurate results; this necessarily depends on the phosphorus-content. My attention has been drawn to an appreciable disagreement between a public laboratory and a works with regard to the figure for the phosphorus-content of a highly phosphoric iron. Erroneous results are also invariably obtained by students for phosphorus in phosphoric irons when issued with samples for analysis of irons of low and high phosphorus-content. This shows that caution is necessary in dealing with irons containing a large amount of phosphorus.

Occasional errors are apparently due to (i) the addition of insufficient molybdate reagent to precipitate the whole of the phosphorus on a 2-grm. sample; (ii) failure to ascertain the approximate phosphorus-content before proceeding with a quantitative method; (iii) the addition of insufficient lead acetate reagent to precipitate all the molybdenum in the "yellow" precipitate, owing to an unsuitable fraction of the ammoniacal solution being taken for the method.

The following procedure is recommended for the analysis of phosphoric irons: An unduly large "yellow" precipitate by the usual method (2-grm. sample) being the first indication of a very high phosphorus-content, it is advisable to recommence the determination on a 0·5-grm. sample. The phosphorus is converted into ammonio-phosphomolybdate in the usual manner (*supra*), but the addition of electrolytic iron to make a larger sample is omitted. Thirty c.c. of the molybdate reagent recommended by Etheridge (*loc. cit.*) are sufficient to precipitate the phosphorus in 0·5-grm. samples of all commercial irons, but may be insufficient when a larger sample is used. An approximate determination for phosphorus is then made by titrating the precipitate with strong solutions of sodium hydroxide and sulphuric acid.* One c.c. of H_2SO_4 = 0·0005 grm. of phosphorus (0·10 per cent. on 0·5-grm. sample), the latter is taken as standard. The range of a 50-c.c. burette covers the phosphorus-content of all commercial irons. The phosphorus being approximately known, a determination is carried out on 0·5-grm. sample, the element being converted into ammonio-phosphomolybdate in the usual manner.

* Approximately 10·7 c.c. of H_2SO_4 (sp.gr. 1·84) per litre. This is standardised by means of a high phosphorus iron of known phosphorus-content, and checked by the addition of pure sodium phosphate to an iron of known phosphorus-content.

The interference of arsenic, titanium, etc., is not of such consequence as in low phosphorus irons, owing to the smallness of the sample used, but if present in appreciable amounts, they are removed by the usual methods prior to the formation of the "yellow" precipitate. This is then treated by alkalimetric titration, or is converted into lead molybdate by the well-known method, in which the addition of at least 15 c.c. of 4 per cent. lead acetate solution is advised. When the phosphorus is known to be greater than 0·5 per cent. the "yellow" precipitate is dissolved in ammonia, the solution is made up to a volume of 100 c.c., and a suitable fraction of this solution is taken as follows:

Approximate phosphorus-content Per Cent.	Fraction required from 100 c.c. volume c.c.	Maximum weight of lead molybdate obtained Grm.
Up to 0·5	100	0·36
0·5 ,, 1·0	50	0·36
1·0 ,, 2·0	25	0·36
2·0 ,, 4·0	10	0·29

This method will yield a precipitate that is quite convenient for filtering off, washing, etc., and it has given satisfactory results in the determination of phosphorus in all basic irons.

B. JONES

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Official Appointments

THE Minister of Health has approved the following appointments:

F. G. D. CHALMERS as a Public Analyst for Leamington Spa, in addition to W. J. Rigby, who becomes Senior Analyst, in place of A. Bostock Hill (deceased) (January 6th, 1933).

HAROLD LOWE as Public Analyst for the Borough of Shrewsbury, in place of A. Bostock Hill (deceased) (January 17th, 1933).

W. J. RIGBY as a Public Analyst for the Borough of Warwick, in place of A. Bostock Hill (deceased).

F. G. D. CHALMERS as Additional Public Analyst for the Borough of Warwick (January 28th, 1933).

H. AMPHLETT WILLIAMS as Public Analyst for the Metropolitan Borough of Woolwich, in place of W. R. Smith (deceased) (January 28th, 1933).

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(From the beginning of the year 1921 *to date)*

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T. H. P.

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 LEICESTER

REPORT OF THE CITY ANALYST FOR THE YEAR 1931

OF the 2023 samples examined, 1388 were samples taken under the Food and Drugs (Adulteration) Act, and 75 of these were adulterated or did not comply with Regulations.

MILK CHEESE.—It was considered quite in order in 1931 for reputable Leicester firms to sell as "Milk Cheese" substances having the following composition:

Water Per Cent.	Fat Per Cent.	Protein Per Cent.	Fat on total solids Per Cent.
78·7	0·20	16·75	1·0
79·0	0·48	15·6	2·3
77·2	0·10	18·1	0·4
77·8	0·17	16·7	0·8

The price charged was similar to that charged for ordinary cheese (10d. per lb.); it was not possible to secure convictions.

SAGO AND TAPIOCA.—In four cases out of nine tapioca was supplied when sago was asked for. Although both articles are permitted to contain up to 100 parts per million of sulphur dioxide, the samples of genuine sago were free from sulphite, whereas all the tapioca examined contained it. A letter was sent to the Council of the local Grocers' Association, and they agreed that the practice of selling tapioca as sago was wrong and should cease. A period of grace in which all the members of the Association could be communicated with was allowed.

SULPHUROUS ACID IN THE ATMOSPHERE.—During and since November determinations of the sulphurous acid present in the atmosphere have been regularly made. According to the figures obtained in November and December, the concentration of sulphurous acid in the air is almost nil in the open country, and only about three parts per 100,000,000 in the outer suburbs. In the centre of Leicester it is highest during the day (average value in November 33·0 parts per 100,000,000), falls off consistently during the night (14·0 parts per 100,000,000), and reaches a comparatively low figure of six to seven during week-ends. The amount of sulphurous acid in the atmosphere reaches its maximum during foggy weather (80·0 parts per 100,000,000 recorded on morning of 17th December, 1931), and tends to be reduced to some extent by rain and to a greater extent by wind.

F. C. BULLOCK

METROPOLITAN BOROUGH OF STEPNEY

ANNUAL REPORT OF THE BOROUGH ANALYST FOR THE YEAR 1931

OF the 1707 samples submitted, 1549 were samples of food and drugs, including 891 formal and 597 informal samples, in addition to "appeal-to-the-cow" cases. Forty-three of the samples were adulterated.

SAMPLING OF PASTEURISED MILK.—Legal proceedings were taken against the contractor of milk supplied to the Mile End Hospital. The sample contained 109,800 bacteria per c.c., and the coliform bacillus was present in 0·00001 c.c. The test for the coliform bacillus is not required for pasteurised milk, so that this evidence of the unsatisfactory nature of the sample could not be produced in Court.

The Magistrate dismissed the summons with £26 5s. 0d. costs against the Council, as in his opinion (1) the milk should have been "mixed or plunged," and (2) the sample should have been packed in ice during transit from the hospital to the laboratory.

With regard to the first point, the inspector was satisfied that the milk was thoroughly mixed by shaking, and this was confirmed by the chemical analyses. With regard to the second point, the Magistrate disregarded the provision in the Regulation: "This precaution may be dispensed with only if the bacteriologist considers it unnecessary on account of the proximity of the laboratory to the place in which the samples are collected."

This point is of importance, since it is clear, from the Regulations, that packing in ice is necessary only when the sample has to be despatched by train or other means from the farm or dairy where the sample is taken. In reply to a request for a ruling on this point, the Ministry of Health stated that if the sample is taken locally, the principle to be observed was that the milk at the time of examination should be in approximately the same condition as the remainder of the consignment when delivered to the consumer, and in such circumstances no special precautions, such as the packing of the sample in ice, should be necessary.

In a similar case at Camberwell, where the same wholesaler was summoned for selling pasteurised milk containing an excessive number of organisms, the case was dismissed on the grounds that the method adopted in taking a sample was not calculated to give a correct indication of the bulk.

In order to meet this difficulty when sampling churns and to comply with the decision of the magistrate that the milk must be plunged, I have devised a sampling outfit consisting of a copper box containing (1) a collapsible plunger which can be extended without touching with the hand (except the handle); (2) a sampling tube fitted in a case to sample beneath the surface; (3) a sample bottle in case. The complete outfit is sterilised and carried to the place of sampling. Churns, however, must be opened before a sample can be taken, but the amount of contamination, in a still atmosphere during the time of plunging, by organisms of the type which will grow on the prescribed medium (agar at 37° C.) may be regarded as negligible. The sample is placed in a refrigerator until the examination is made.

Sulphur Dioxide in Biscuit Meal in Sausages.—Two samples of sausages from the same vendor were found to contain 13 parts of sulphur dioxide per million and did not bear the required declaration. The vendor stated that no preservative had been added, and that biscuit meal was an ingredient of the sausages. It is probable that the small amount of sulphur dioxide found had been introduced in this way.

Proceedings against Wholesaler.—Two samples of ground ginger from the same vendor contained 370 parts of sulphur dioxide per million. Proceedings were taken against the retailer and the wholesaler. The retailer, who stated that the boxes containing the ground ginger were marked "Finest Ground Ginger, Genuine," and produced an invoice relating to the sale, was unable to prove a warranty, and he was fined £2 with £10 10s. 0d. costs. It was contended for the wholesaler that no sample had been taken from him and he had not received any portion of any sample taken. The magistrate dismissed this summons with £10 10s. 0d. costs against the Council.

Article 7 of the Public Health (Preservatives, etc., in Food) Regulations states that "the authority may, instead of, or in addition to, taking proceedings against the seller, take proceedings against any previous seller of the article notwithstanding that the sale by such previous seller took place outside the district of the authority."

The Council appealed against the decision of the magistrate. The Court held that Article 6 relating to the division of the sample applied only to samples taken where articles of food were actually manufactured and not to proceedings taken under Article 7 against a previous seller, that Article 7 referred to "*the* article," and that it was a case where a sample had already been taken and analysed, and that the previous seller was in no worse position than the giver of a warranty under the Food and Drugs Acts. The appeal was allowed with costs, and instructions were given to convict. The wholesaler was later fined £1 with £5 5s. 0d. costs.

Douglas Henville

Queensland

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDING JUNE, 1932

In his Annual Report the Queensland Government Analyst (Dr. J. B. Henderson) states that the number of samples analysed during the year (9725) formed a record, being an increase of 1139 over the previous year. Of the 3431 samples analysed for the Department of Public Health, 1921 were legal samples taken in accordance with the Health Acts.

Milk.—There were 1865 legal samples of milk, of which 1500 passed the standard. Of the 145 samples deficient in fat, 69 were from Brisbane. The removal of fat from milk is just as prevalent as ever. The average proportion of fat in all milk samples during the last 30 years has varied from 3·9 to 4·1 per cent. There is, therefore, no excuse for about one sample in every thirteen falling below the legal minimum of 3·3 per cent. of fat.

Lead Arsenate in Vegetables.—Thirty-two samples of cabbage and six samples of cauliflower contained lead arsenate. One cauliflower contained about 13 grains on the leaves and seven-tenths of a grain on the flower. Although the position has much improved, a few growers still persist in the dangerous practice of using lead arsenate.

Lead in Paints, Crayons and Stamping Inks.—Of 21 samples of paint scrapings submitted, 14 contained more than 5 per cent. of soluble lead. The use of such paints on any verandah railing, gate or fence is prohibited.

Nine boxes of crayons were examined in regard to their suitability for use in schools. Lead chromate was present in the orange-yellow and green crayons, and these were reported to be unsuitable for use by children.

Two of 20 marking inks used for branding food containers were found to contain lead compounds.

Toxicological Work.—In 32 out of 53 cases poison was detected. Strychnine was found in connection with 19 cases, cyanide in 4 cases, arsenic in 3, carbon monoxide in 3, cresol in 2, and sodium fluoride in one case.

Wheat Act, 1932

DEFINITION OF BREAD, FLOUR, MEAL, ETC.

This is an Act to secure to growers of home-grown millable wheat a standard price and a market therefor; to make provision for imposing on millers and importers of flour obligations to make payments calculated by reference to a quota of such wheat and as to disposal of the moneys thereby received; to provide for such millers being required to purchase unsold stocks of such wheat, and for purposes connected with the matters aforesaid.*

The Act comprises 21 sections and two schedules, the first dealing with the Constitution and Proceedings of the Wheat Commission, and the second with the Constitution and Proceedings of the Flour Millers' Corporation.

In section 20, which deals with the interpretation of the expressions used in the Act, the following definitions (*inter alia*) are given in subsection (1).

"Bread" means the product produced by baking flour unmixed with any substance other than water, salt and yeast or other leaven, so, however, that no such product shall be deemed to be bread unless it is in the form of a loaf weighing not less than fourteen ounces.†

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* [22 & 23 Geo. 5, Ch. 24]. May 12, 1932.

† When the Wheat Bill was before Parliament and the Home Secretary (Sir John Gilmour) moved the insertion of this definition for bread, attention was called by the Member for Bermondsey to the fact that malt extract and other substances were often used in making bread. In his reply, the Home Secretary said (see *Times*, April 8th, 1932): "In England the customary weight of the loaf was 16 oz., but in Scotland and Northern Ireland it was 14 oz. As to the point raised by Dr. Salter about the addition of malt and other flour-raising ingredients (*sic*), the definition, he was advised, included substances such as improvements (*sic*)."

"Flour" means the products produced by the milling of wheat, and includes all such products except substances separated in the milling as wheat offals, and (subject to the provisions of subsection 2 of this section) where such products as aforesaid are mixed with other substances, whether or not produced by the milling of wheat and whether milled with the wheat or subsequently added, the mixture shall be deemed to be flour.

"Meal" means wheat meal as defined by the Fourth Schedule to the Fertilisers and Feeding Stuffs Act, 1926, either alone or mixed with other substances not being flour.

"Millable wheat" means wheat which conforms to the standard prescribed by regulations made by the Minister.

"Wheat offals" means the residual products which, in the process of milling wheat, are extracted therefrom as germ or for animal or poultry food.

(2) Notwithstanding anything in the definition of flour contained in the last foregoing subsection—

(*a*) Where any flour consists of a mixture containing substances not produced by the milling of wheat, by-laws of the Wheat Commission made in that behalf may direct that, as respects that mixture, those substances shall be deemed not to form part of the flour.

(*b*) If in any parcel containing substances produced by the milling of wheat the weight of those substances, other than wheat offals, does not exceed seven and a half per cent. of the weight of the parcel, the parcel shall be deemed not to contain flour.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Formation of Volatile Fatty Acids on Exposure of Rye and Wheat Oils to the Atmosphere. S. C. L. Gerritzen and M. Kauffman. (*Chem. Weekblad,* 1932, **29**, 742–745.)—Exposure of the oils from rye and wheat in thin layers for 8 weeks at room temperature produces appreciable quantities of volatile fatty acids which are partly soluble in water, form insoluble silver salts, and have a mean molecular weight ranging from 80 to 117; traces of caproic, butyric and acetic acids were detected. Attempts have been made to follow the changes under different experimental conditions from the variations in the Reichert–Meissl value (which increases in some cases from 0·6 to 16), the Kirschner value (0·2 to 12), and the Polenske, acid, and saponification values. These indicate that exposure in the dark and sterilisation stimulate the changes, dry sterilisation for 1 hour at 110° C. being the most effective, and wet sterilisation the least. Exposure in an atmosphere of carbon dioxide tends to inhibit the change. The influence of light on the micro-organisms occurring in wheat and rye, and on the saponification value, is discussed. J. G.

Two New Colour Tests for Hexoses. J. H. Foulger. (*J. Biol. Chem.,* 1932, **99**, 207–211.)—A urea, stannous chloride and acid reagent which gives definite colour reactions with simple hexoses also differentiates between ketohexoses and aldohexoses. The reagent, which keeps well, is prepared by dissolving 40 grms. of urea in 80 c.c. of 40 per cent. (by vol.) sulphuric acid, adding 2 grms. of stannous chloride and boiling until clear. On cooling, the volume is made up to 100 c.c. with 40 per cent. acid. The sugar solution to be tested (0·5 c.c.) is mixed with 3 c.c. of the reagent, and the mixture boiled for about 45 seconds and then shaken. A green-blue colour, increasing in intensity on cooling, appears in the

presence of a ketohexose, whilst an aldohexose gives a yellow or olive-green colour, becoming amethyst on alternate boiling and shaking. Furfural and pentoses give an intense yellow coloration, and the disaccharides give the colours of the simple sugars of which they are composed, but with rather greater difficulty; maltose and lactose give the amethyst coloration of glucose, inulin the blue of laevulose, and sucrose an intermediate colour. The lower limits of sugar concentration for the appearance of the colour are: laevulose, 0·02 mgrm., and glucose, mannose or galactose, 0·5 mgrm., in 3·5 c.c. of solution. A guanidine reagent is made by dissolving 25 grms. of guanidine in 80 c.c. of 40 per cent. (by vol.) sulphuric acid, diluting the solution to 100 c.c. with acid, and saturating it with stannous chloride. It gives a colour with each sugar, different from those obtained with the urea reagent. When the sugar solution (0·5 c.c.) is boiled for one minute with 3 c.c. of the reagent, the simple hexoses give a colour which is just perceptible with 0·1 mgrm. in the 3·5 c.c. of mixture. Laevulose gives a distinctly red hue, mannose a somewhat yellower red, glucose a blue-red, and galactose a bluer colour than laevulose or mannose, but yellower than that with glucose. Pentoses and furfural give only a yellow colour. D. G. H.

Nature and Composition of the Mucilage of the Seed of White Mustard (*Brassica Alba*). K. Bailey and F. W. Norris. (*Biochem. J.*, 1932, **26**, 1609–1623.)—The gums and mucilages are complex colloids which are not infrequently found to be mixtures of almost equally complex substances of closely similar physical and chemical properties. Separation of the constituents is consequently difficult, and, after separation, the characterisation of the components is not an easy matter. The object of this investigation of the mucilage of mustard seed was not solely the identification of the products of hydrolysis, but also the separation of the product into definite fractions. The fractionation was not based on physical properties, but was effected by the action of alkali. Full experimental details of the investigation are given, and the results are summarised as follows: The mucilage of mustard seed is shown to consist of a complex of cellulose and acid polysaccharides. The cellulose may be readily separated by warming with dilute sulphuric acid. By addition of barium hydroxide solution to the mucilage solution a gel, and also a soluble fraction composed of rhamnose, arabinose, galactose, and galacturonic acid, are obtained. The gel may be further separated, by the action of 4 per cent. sodium hydroxide solution, into cellulose and a fraction composed of arabinose, galactose, galacturonic acid and glycuronic acid. The acid polysaccharides contain methoxyl groups in ether-linkage. Aldobionic acids, probably rhamnose- and galactose-galacturonic acids, are present in the mucilage. A peroxidase system is present in cells situated close to the mucilage-secreting cells, and may be responsible for the production of uronic acid residues from pre-existing hexosan material. P. H. P.

Reactions for Caffeic Acid and Chlorogenic Acid. W. Hoepfner. (*Chem.-Ztg.*, 1932, **56**, 991.)—*Caffeic Acid* (a primary decomposition-product of chlorogenic acid): A solution in dilute acetic or phosphoric acid assumes an intense cinnabar-red colour, which changes to orange on dilution; the sensitiveness is 1:100,000. *Chlorogenic Acid.*—The fat is removed from 5 grms. of ground raw

coffee-beans by extraction for 30 minutes with boiling acetone, and the dry residue is then digested for some hours in 50 c.c. of a concentrated solution of sodium chloride. This mixture is diluted to 100 c.c. and is boiled for 15 minutes, the liquor being then separated by decantation, and the residue is again boiled with 50 c.c. of water. This process of decantation and boiling is repeated 4 or 5 times (the chlorogenic acid being thus extracted almost quantitatively), and the solution is finally diluted to 250 c.c. and filtered while warm. The clear filtrate, or an aliquot portion diluted to 125 c.c., is shaken with 0·5 c.c. of a saturated solution of sodium nitrate, and 7 grms. of urea, and then 0·5 c.c. of concentrated acetic acid are added. After 3 minutes a carmine-red colour is developed by the addition of 5 c.c. of sodium hydroxide solution (*i.e.* excess, strength not stated), and, as a qualitative reaction, this is sensitive to 1:100,000; alcohol or larger quantities of urea decrease the sensitiveness. The reaction may be made quantitative by an examination of the absorption spectrum of the diluted solution in a photometer; the principal bands are at 610 and $570m\mu$. Alternatively, a comparison with a solution of pure chlorogenic acid may be made. A typical figure for the content of chlorogenic acid in a number of coffees is about 7·5 per cent. J. G.

Determination of Theobromine in Pharmaceutical Preparations by Boie's Method. H. J. Van Giffen. (*Pharm. Weekblad*, 1932, **69**, 1321–1325.)—Boie's method (*Pharm.-Ztg.*, 1930, **75**, No. 67) has been found satisfactory, and is more generally applicable than the method of the Dutch Pharmacopoeia. A solution of 500 mgrms. of the sample in 100 c.c. of water is warmed with 15 c.c. of 0·1 *N* sulphuric acid at 40° C. in order to remove carbon dioxide, and 1·5 c.c. of a solution of phenol red (0·1 grm. in 5·7 c.c. of 0·05 *N* sodium hydroxide solution and 500 c.c. of water, stored in a bottle which is protected from contamination by carbon dioxide) are added. A measured quantity (*e.g.* 2 to 3 c.c.) of 0·1 *N* sodium hydroxide solution is then added until the mixture is alkaline, followed by 0·1 *N* sulphuric acid until the colour changes from deep red to lemon-yellow; the alkalinity of the sample may then be calculated. A mixture of the resulting solution with 20 c.c. of 0·1 *N* silver nitrate solution is then titrated with the 0·1 *N* alkali until the deep red-violet colour is again attained, when the theobromine present may be calculated from the equation $C_7H_8N_4O_2 + AgNO_3 \rightleftharpoons C_7H_7N_4O_2Ag + HNO_3$ (1 c.c. of alkali $\equiv$ 18·01 mgrms. of theobromine); the approach of the end-point is indicated by incipient precipitation of silver oxide. This method is suitable for (*e.g.*) *Salicylas natricus cum Theobromino-Natrio*, but must be modified in certain other cases. Thus, with *Acetas natricus cum Theobromino-Natrio*, the powdered sample is first evaporated in a dish with 35 c.c. of 0·1 *N* sulphuric acid until the odour of acetic acid is no longer apparent; other details are given for several other preparations of theobromine. The results deviate from those obtained by the Kjeldahl method by +0·5 to −1·0 mgrm., but are 6 to 10 mgrms. higher than those obtained by the Pharmacopoeia method. J. G.

Biochemical

Iron and Copper in Liver and Liver Extracts. A. E. Mayer and C. Eggert. (*J. Biol. Chem.*, 1932, **99**, 265–270.)—Iron was determined in certain liver and liver extracts by the Elvehjem and Peterson method (*J. Biol. Chem.*,

1927, **74**, 433), and copper by the Elvehjem and Lindow modification of the Biazzo method (*J. Biol. Chem.*, 1929, **81**, 435). Horse, hog, and dog livers were found to be uniformly high in iron, bullocks' livers containing considerably less, but, on the other hand, bullocks' livers contained the highest proportion of copper. Only a proportion of the metals (perhaps hardly more than half) are soluble in water, but the precipitate obtained with 67 per cent. alcohol carried almost all the iron and the greater part of the copper. Proportions of iron (calculated on the dry substance in the whole livers) were as follows: Horse, 0·08; dog, 0·10; hog, 0·09; bullock, 0·02 per cent., and copper (as mgrms. per kilo. of dry substance in the whole livers): Horse, 28; dog, 44; hog, 16; bullock, 57. D. G. H.

Calcium-Content of Cabbage. S. J. Cowell. (*Biochem. J.*, 1932, **26**, 1422–1423.)—During some experiments on the calcium balances of rabbits receiving a small daily allowance of cabbage it was considered advisable to determine the amount of calcium in the leaves taken from different parts of the plant. The variations found were so large that even when as little as 10 grms. of cabbage a day were given and the rest of the daily diet contained 150 mgrms. of calcium, calculations of the balances might be completely fallacious if leaves from one part of the plant were taken for analysis, and leaves from a slightly different part of the plant were given to the animals to eat. Samples of the leaf of cabbages obtained from Covent Garden Market in June were weighed moist, ashed, and tested for their calcium-content. The following are typical of the results obtained: (i) Outer dark green leaf, 476; inner pale green leaf, 35; (iv) Outermost, dark green leaf 1058; third leaf (dark green), 216; inner leaf (pale greenish-yellow),71; heart leaf (yellowish-white), 32 mgrms. per 100 grms. of moist leaf. The results show that the calcium-content of the outermost leaves of the cabbage in summer may be from 20 to 30 times as great as that of the inner leaves. A daily ration of 10 grms. of cabbage may supply anything up to 100 mgrms. of calcium, and there may be a five-fold variation in the calcium-contents of leaves from the same plant which are indistinguishable in appearance. It is of interest to note that the outermost leaves of the particular cabbages used for the determinations are richer sources of calcium than any other common food, with the possible exception of cheese; although such leaves are discarded by man, they are usually preferred by the rabbit. P. H. P.

Colorimetric Determination of Histidine. E. Jorpes. (*Biochem. J.*, 1932, **26**, 1507–1511.)—The colorimetric determination of histidine by the reaction of Pauly (*Z. physiol. Chem.*, 1904, **42**, 508) has been studied. By means of the Zeiss photometer the development and the stability of the colour were followed. It was found that the procedure recommended by Hanke and Koessler (*J. Biol. Chem.*, 1919, **39**, 497, 1920, **43**, 527; ANALYST, 1920, **45**, 454), which has been largely applied during recent years, gives very unsatisfactory results. However, with the use of their reagents, and by changing the technique, it is possible to get easily reproducible figures. A true proportionality is obtained between the intensity of the colour and the amount of histidine present in the range 0·05 to 0·005 mgrm. of histidine per c.c. The technique is as follows:—*Solutions.*—(1) A neutral or faintly acid histidine solution containing 0·05 to 0·005 mgrm. of histidine per c.c. (2) A diazonium solution prepared as described by Hanke and

Koessler. To 1·5 c.c. of a solution containing 0·9 grm. of sulphanilic acid and 9 c.c. of concentrated hydrochloric acid in 100 c.c. are added 1·5 c.c. of a 5 per cent. sodium nitrite solution. The mixture is cooled on ice for 5 minutes. Then 6 c.c. of the nitrite solution are added with shaking, the mixture is cooled for 6 minutes, and water is added to 50 c.c. thereof. The diazonium solution can be kept on ice for 24 hours. The solution of sulphanilic acid keeps for years. The sodium nitrite solution should be freshly prepared. (3) A 1·1 per cent. solution of anhydrous sodium carbonate. *Procedure.*—To 1 c.c. of the histidine solution are added 2 c.c. of the diazonium solution. After 1 to 3 hours 5 c.c. of the carbonate solution are added. The reading is made with filter S.50 of the step-photometer 4 to 8 minutes after the addition of the carbonate. The amount of histidine present in the specimen is calculated from the figure found for ϵ or $-\log_{10}\frac{I_p}{I_a}$. If 1 c.c. of the solution, or 8 c.c. of the reaction mixture, contain 0·1 mgrm. of histidine the figure for $-\log_{10}\frac{I_p}{I_a}$ is 2·66, *d* being 1 cm. Almost the same figure for ϵ was obtained on three different occasions with a 3 to 6 months' interval, *viz.* 2·66, 2·69 and 2·66. The colorimetric method, thus modified, is recommended for the determination of histidine in the basic fraction of the amino-acids in the protein analysis according to Van Slyke. This reaction, with the given technique, seems to be the most trustworthy of all the quantitative colorimetric reactions for amino-acids, due regard being given to its non-specificity in the presence of tyrosine, guanine, adenine, phenols, iminazoles, sulphides, and ammonium salts. P. H. P.

Use of the Sakaguchi Reaction for the Quantitative Determination of Arginine. E. Jorpes and S. Thorén. (*Biochem. J.*, 1932, **26**, 1504–1506.)—The reaction of Sakaguchi (*J. Biochem.* (*Japan*), 1925, **5**, 25) with α-naphthol and hypobromite has been used for the determination of arginine in protein hydrolysates. Weber (*J. Biol. Chem.*, 1930, **86**, 217) showed that the reaction can be used for the quantitative determination of 0·05 to 0·005 mgrm. of arginine. The details of this colorimetric procedure have been studied. Instead of a colorimeter, a Zeiss step-photometer was used. If the necessary precautions are taken, the reaction can be used for quantitative purposes. The modified technique is as follows:—*Solutions required.*—(1) An arginine solution containing 0·04 to 0·07 mgrm. of arginine in 5 c.c.; (2) a 10 per cent. solution of sodium hydroxide *e natrio*; (3) a 0·02 per cent. solution of α-naphthol, freshly made each time by the dilution of 20 c.c. of a stock solution (0·1 per cent. in alcohol) to 100 c.c. with water; (4) a hypobromite solution made by dissolving 2·5 grms. (0·46 c.c.) bromine in 100 c.c. of 5 per cent. cooled sodium hydroxide solution; this solution keeps for months in the cold; (5) a 40 per cent. urea solution. *Procedure.*—A test-tube, 150 × 18 mm., with 5 c.c. of arginine solution is cooled on ice, then 1 c.c. of the sodium hydroxide solution is added, and 1 c.c. of the α-naphthol solution, the solutions are mixed, and the test-tube is well embedded in ice. After a time (1 hour) 0·2 c.c. of the hypobromite solution is added with vigorous shaking, and, exactly 15 seconds

later, 1 c.c. of cooled urea solution. The photometric reading is made against water in S.50 (see preceding abstract) within 6 to 8 minutes. For amounts of arginine between 0·04 and 0·08 mgrm., which is the range found to be most convenient in these experiments, a 0·5 cm. dish is used. The amount of arginine present is found directly from a curve on semi-logarithmic paper. The amounts of arginine taken in a standard series are used as abscissae and the photometer scale as the logarithmic ordinates. The points fall on a straight line, and thus no further calculation is required. If the cooling is not sufficient, another line may be obtained. It is advisable each time to have controls of different concentrations in order to check this. Duplicates agree to within 1 to 2 per cent. The method is also applicable to the determination of the arginine-content of the basic fraction of the amino-acids in the Van Slyke procedure. P. H. P.

The *o*-Benzoquinone Test for Cysteine. W. C. Hess and M. X. Sullivan. (*J. Biol. Chem.*, 1932, **99**, 95–97.)—A study of the Dyer and Baudisch test for cysteine (formation of a deep red coloration in the chloroform layer when an aqueous solution of cysteine hydrochloride is shaken with a chloroform solution of *o*-benzoquinone) shows that, although amino-acids and various sulphur compounds give a negative result, and the test differentiates cysteine from these, yet benzidine, aniline, anthranilic acid, indole (in 40 per cent. alcohol), cystine amine hydrochloride, aminoguanidine carbonate, *iso*-amylamine, *n*-propylamine, *n*-butylamine, disulphide of dithiotyrosine (after reduction), chloroacetylcystine (after reduction), trimethylamine and acetonitrile all give red colours. Glutathione considerably interferes with the reaction. The Sullivan reaction (with 1,2-naphthoquinone-4-sodium sulphonate in a reducing atmosphere) is more nearly specific, and requires that the three groups of cysteine, $-SH$, $-NH_2$, $-COOH$ be free, and in the order occurring in natural cysteine. D. G. H.

Cerevisterol, a Sterol Accompanying Ergosterol in Yeast. E. M. Honeywell and C. E. Bills. (*J. Biol. Chem.*, 1932, **99**, 71–78.)—Cerevisterol has been isolated from the mother liquors remaining from ergosterol manufacture, some of the substance separating from the final crop of crystals, but a large part remaining in the oily liquor. The crude cerevisterol is separated from the liquor by adding an equal volume of hexane, and, after one week, crystallising the amorphous precipitate once or twice from acetone, and many times from alcohol-acetone (1:3). Eventually 10 grms. of the pure product were obtained from 4500 kilos. of dry yeast. The substance (probable formula $C_{28}H_{47}O_3$) is remarkably stable, and after several weeks' exposure showed no discoloration and no change in its m.pt. of 265·3° C. From alcohol it crystallises in elongated prisms, or from acetone or ethyl alcohol in broad hexagonal prisms. The product showed $[\alpha_\lambda]^{25°}_{5461} = -57{\cdot}4°$ in chloroform, and a weak absorption band at $248 m\mu$. No antirachitic properties developed on irradiation. It has two double bonds, one apparently the $\Delta^{1,2}$ (or $\Delta^{1,13}$) linkage of ergosterol and *iso*-ergosterol, and two hydroxyl groups, whilst the nature of the third oxygen atom is undetermined. The angles adjacent to the long sides of its crystals measure 124°, and those between the short sides 112°. Cerevisteryl diacetate melts at 171° C., and has $[\alpha]^{25°}_{5461} = -163°$. D. G. H.

Determination of Vitamin *A* in Cod-Liver Oils, (A) Biologically, (B) Chemically, (C) Physically, with a Statistical Examination of the Results. II. Further Evidence that the Intensity of Absorption at 328$m\mu$ gives best Agreement with Biological Measure of Vitamin *A* in Cod-Liver Oils. K. H. Coward, F. J. Dyer and R. A. Morton. (*Biochem. J.*, 1932, **26**, 1593–1600.)—It was shown by Coward, Dyer, Morton and Gaddum (*Biochem. J.*, 1931, **25**, 1102; ANALYST, 1931, **56**, 821) from an examination of eleven samples of cod-liver oil and two concentrates that, taking into account the known sampling error of the biological test, the measurement of the absorption by the oil at 328$m\mu$ gave the best agreement with the vitamin *A* value as determined by a biological test. The "blue value" of the unsaponifiable fraction of the oil did not agree so well, whilst the "blue value" of the oil itself gave only a very crude measure of the biological activity. It was pointed out, however, that the intensity of absorption of certain oils lay outside the range of the possible biological value. The results of all the tests were evaluated by means of a curve and expressed in terms of the oil A originally used for the making of the curve. It was decided to test certain oils again by making a simultaneous test on oil A and using "litter-mate" animals in the groups. The re-examination of four oils and the examination of five further samples of cod-liver oil by the biological, chemical and physical methods indicate again that the intensity of absorption at 328$m\mu$ by the oil itself gives the best measure of the vitamin *A* value of the oil. In the re-testing of the old oils, the blue value of the unsaponifiable fraction again agreed better with the biological value of the oil than did the blue value of the oil itself, but in the tests made on freshly prepared oils there was no evidence that any one method of measuring the blue value was better than the rest; they all gave approximately the same results. Some evidence is given that a more accurate determination of vitamin *A* in an unknown oil in relation to a given (standard) oil is obtained if a simultaneous test on the standard is made and the respective responses compared, than if the response to the unknown is compared with an average response of the standard. P. H. P.

Bacteriological

Fermentation of Cellulose by Thermophilic Bacteria. Y. Tomoda. (*J. Soc. Chem. Ind. Japan*, 1932, **35**, 534B.)—A thermophilic cellulose-decomposing bacterium has been isolated from a manure heap by repeated cultures at 65° C., in a medium consisting of peptone (5 grms.), calcium carbonate (20 grms.), sodium ammonium hydrogen phosphate (2 grms.), potassium dihydrogen phosphate (1 grm.) magnesium sulphate (0·3 grm.), sodium chloride (0·1 grm.), filter-paper (20 grms.), and tap water (1000 grms.). It is a long mobile rod resembling *Clostridium thermocellum*. After 48 hours the filter-paper loses its structure, and the attached fibres are only 0·5 mm. in length and have sharp ends. These bacteria readily ferment raw or refined cotton wool, and, to a smaller extent, viscose silk, newspaper, and sulphite pulp, but cannot ferment leaves, sawdust, nitrocellulose or acetyl cellulose.

On investigating the chemical properties of filter-paper at intervals during fermentation, no change was observed in the copper number, viscosity in

cupro-ammonium solution or content of α-, β- or γ-celluloses—a marked contrast to the change undergone by acid hydrolysis.

The readiness with which various types of cellulose were fermented was found to be in the following decreasing order:—Undried, pasty cotton cellulose, cotton wool, filter-paper, and sulphite wood pulp, mercerised cotton wool, viscose silk, cellophane, acetate silk and nitrocellulose (the last three do not ferment at all). It is considered that fermentability depends on microscopical rather than on colloidal structure, a porous structure being more easily accessible to bacterial attack than a smooth surface and compact structure. R. F. I.

Biochemical Study of the Fermentation of Rare Sugars by Members of the Colon-Aerogenes Groups of Bacteria. I. Trehalose. C. F. Poe and J. T. Field. (*J. Biol. Chem.*, 1932, **99**, 283–287.)—The cultures used were members of the *Escherichia* and *Aerobacter* groups of bacteria, and the medium for the determination of hydrogen ion concentration and the qualitative gas production was prepared by dissolving 1 grm. of trehalose and 8 grms. of "Bacto-Nutrient" broth in 1 litre of water; this was adjusted to p_H7, and 10 c.c. were placed in Durham fermentation tubes which were then sterilised. For quantitative determinations, 5 grms. of trehalose and 8 grms. of "Bacto-Nutrient" were dissolved in 1 litre of water; 100-c.c. amounts in 250-c.c. flasks were used, and 50-c.c. amounts were sterilised in Smith fermentation tubes. The p_H values and gas readings were practically the same for both the colon and aerogenes group. In the medium containing 0·1 per cent. of sugar the p_H values reached a minimum in about 7 hours, thereafter gradually increasing to about 8·7. The minimum was much lower for the medium containing 0·5 per cent. of sugar, and the acidity developed killed the organisms in about 60 hours. The analyses of the gases and fermentation products showed that the aerogenes group produced a larger amount of each constituent except succinic acid, and of this acid the colon group formed twice as much. The ratio for acetic to succinic acid was greater, and that for acetic to lactic acid less, for the aerogenes than for the colon group. D. G. H.

Toxicological and Forensic

Hydrogen Arsenide Poisoning due to the Action of Water on Metallic Arsenides. R. R. Bomford and D. Hunter. (*Lancet*, 1932, **223**, 1446–1449.)—The two cases of poisoning here reported were of men working near a plant in which experiments on the refining of tin were being made. Metal foil, composed of tin, aluminium, and lead, was added to a melt of tin, antimony, copper, arsenic (0·1 per cent.), and lead. The dross which rose to the surface and contained, *inter alia*, aluminium arsenide, was placed in a heap before the pot and, to lay the dust being formed, was sprinkled with water while still hot. The operatives of this process were unharmed, but two others who were ten yards away and in the line of a draught from the heap of dross, were affected by severe arsenic poisoning. The dross was found to contain 0·5 per cent. of arsenic. Means are suggested for rendering such operations safe, and it is considered that greater publicity should be given to the danger attending the action of water on aluminium arsenide. Previous cases of this nature have been published only in the reports of the Chief Inspectors of Factories. T. H. P.

Organic Analysis

Determination of Halogens in Organic Compounds by the Sodammonium Method: Determination of Fluorine. F. Govaert. (*Compt. rend.*, 1932, **195**, 1278–1280.)—The method previously given (*ibid.*, 1932, **195**, 797) for the determination of halogens in compounds insoluble in liquid ammonia appears to be of general applicability. With compounds containing fluorine, the ammonia is allowed to evaporate after decomposition of the compound with liquid ammonia and sodium, the residue being taken up in water and the fluorine determined as calcium fluoride. Such resistant compounds as fluorobenzene, trifluorotoluene, and ethyl trifluoroacetate readily yield their fluorine in this way (*cf.* ANALYST, 1933, 49). T. H. P.

Detection and Determination of Fluorine in Organic Compounds. W. Bockemüller. (*Z. anal. Chem.*, 1932, **91**, 81–90.)—A comprehensive review of modern processes for the detection and determination of fluorine in organic compounds is given. The following new methods are described: *Detection of Fluorine.*—The method, which is applicable only to relatively non-volatile compounds, depends on the wet oxidation of the substance with chromic and sulphuric acids in the presence of glass. Ten to 20 mgrms. of the substance (corresponding to about 0·5 mgrm. of fluorine) are dissolved in a test-tube in a few c.c. of concentrated sulphuric acid. Finely powdered potassium dichromate is added and the tube is heated gently. A sensitive indication of the presence of fluorine in the substance is given by a peculiarity of the acid liquid failing to "wet" the glass. As a confirmatory test, a drop of water adhering to a glass rod (which has preferably been smeared with a little fatty material) is brought over the mouth of the tube, when the appearance of a turbidity of silica in the drop indicates the presence of fluorine in the substance. Chlorine compounds interfere with the test owing to the formation of chromyl chloride, which obscures the observation of silica in the drop; this difficulty may be overcome by substituting potassium dichromate by manganese dioxide. *Determination of Fluorine.*—The method consists in burning the substance in a platinum combustion tube in a stream of air charged with ammonia, the function of which is to provide, on its combustion, a convenient source of the water vapour necessary to aid in the quantitative decomposition of certain compounds, *e.g.* carbon tetrafluoride; the hydrofluoric acid produced is absorbed by heated calcium oxide and is determined gravimetrically as calcium fluoride. *Method.*—The combustion apparatus consists of a platinum tube 30 cm. × 10 mm. diameter. An annular copper vessel through which water is passed surrounds the entry end of the tube for the purpose of cooling it. The other end of the tube projects to a distance of about 10 cm. into an electric furnace giving a temperature of 900° C.; this part of the tube is filled with granular calcium carbonate, which is kept in place between plugs of filter-paper. [The method given for the preparation of the granular calcium carbonate is as follows: 20 grms. of pure calcium carbonate are converted to calcium oxide by strongly heating in a platinum dish; the product is powdered and mixed with 200 grms. of calcium carbonate and kneaded into a mass with 75 c.c. of water; the mass is

broken up by shaking it in a beaker into small pellets (2 to 3 mm. diameter), which are kept in an atmosphere of carbon dioxide overnight and finally dried.] The filled end of the tube is heated at 900° C. for half-an-hour, a slow stream of air, which has bubbled through concentrated ammonia solutions, being passed through the tube. The substance to be analysed (100 to 200 mgrms.), contained in a platinum boat, or, in the case of a volatile liquid, a small glass bottle, is introduced into the combustion tube; the boat is pushed to a position in the tube, estimated from the temperature gradient which exists along its length, at which the prevailing temperature is about 50° below the boiling-point of the substance; finally a plug of filter-paper is inserted close to the boat. The slow passage of air (about 1 bubble per second) is continued for 1½ hours, and the combustion is then completed by heating the exposed part of the tube with a Bunsen flame for a short period. After cooling, the combustion tube is emptied, by means of light tapping, into 300 c.c. of "calcium fluoride water" (water saturated at the ordinary temperature with calcium fluoride, employed to compensate for the solubility of calcium fluoride precipitates in water), any material remaining adherent in the tube being removed with the aid of a glass rod. To the suspension, 15 c.c. of glacial acetic acid are added, and the whole is kept at the ordinary temperature with occasional stirring for 15 hours. The insoluble residue is filtered off, washed with about 500 c.c. of the "calcium fluoride water," and ashed in a weighed platinum crucible. The ash is moistened with hydrofluoric acid (in order to reconvert any calcium fluoride hydrolysed in the ashing process), the excess of acid is removed by gentle heating, and the residue is finally ignited and weighed as calcium fluoride. Any chlorine or bromine in the substance may be determined in the filtrate from the calcium fluoride in the ordinary manner. In test experiments good results were obtained for the determination of fluorine in various aliphatic and aromatic compounds. S. G. C.

Determination of Cyanide by Distillation from Acid Solution. H. A. Pagel and W. Carlson. (*J. Amer. Chem. Soc.*, 1932, **54**, 4487–4489.)—Tests have been made of the completeness with which hydrocyanic acid may be recovered from a cyanide solution by distillation with dilute sulphuric acid. The apparatus used comprised a 500-c.c. distilling flask, fitted with a water-condenser leading to a simple absorption apparatus consisting of a wide-necked bottle provided with a two-holed stopper carrying (*a*) as leading tube the stem of an inverted funnel which dips below the surface of the absorbing liquid (15 c.c. of 6 *N* sodium hydroxide solution diluted to 200 c.c.), (*b*) an exit tube connected with an auxiliary absorbing tube of the Péligot type. A known amount of standard potassium cyanide solution was placed in the distillation flask, with or without other salts, the possible effect of which it was desired to test, diluted to about 250 c.c., and acidified with sulphuric acid, the stopper was immediately inserted, and the solution was distilled at a moderate rate for a period of 13 to 15 minutes (60 to 80 c.c. of liquid being distilled), a slow current of air being meanwhile aspirated through the apparatus. The results showed: (*a*) That when the rate of heating up to the distillation temperature was rapid (5 minutes), accurate results were obtained, but that when the rate of heating was less rapid (10 minutes) the results

were, in general, from 0·1 to 0·3 per cent. too low; (*b*) considerable amounts of alkali chloride, bromide, nitrate and sulphate were without interference. In the absence of the auxiliary absorption tube, losses ranging from 0·1 to 0·3 per cent. resulted. The cyanide was determined by titration with silver nitrate by the Liebig-Denigès method. S. G. C.

Determination of Tetramethylammonium. J. J. Bikermann. (*Z. anal. Chem.*, 1932, **90**, 335–337.)—The author's problem was the determination of small quantities (about 0·005 grm.) of tetramethylammonium sulphate or nitrate in presence of several hundred times its weight of sodium sulphate, copper nitrate or silver nitrate, dissolved in about 5 c.c. of water. The following method, which was adopted, depends on thermal decomposition of the base in solution according to the equation

$$(CH_3)_4N.OH = (CH_3)_3N + CH_3.OH,$$

and the distillation and ultimate titration of the trimethylamine formed:—The solution is placed in a nickel retort (40 to 50 c.c. capacity), and 1 grm. of sodium hydroxide is added. The retort is fixed so that the stem slopes upwards; the stem is connected with a glass tube 100 cm. long, to act as a spray trap, which, for part of its length (70 cm.), slopes in line with the stem, and the remainder is bent downwards, and leads to a condenser, the exit end of which is connected with an absorption tube containing 0·05 *N* sulphuric acid. The retort is heated, gently at first, and then more strongly, until almost dull red; it is allowed to cool, 1 c.c. of water is added to the contents, and the heating is repeated. The distillate is back titrated with 0·05 *N* sodium hydroxide solution. In test experiments practically theoretical results were obtained. S. G. C.

Refractometric Measurement of Anti-freezing Mixtures of Ethylene Glycol Type. E. H. Harvey. (*Amer. J. Pharm.*, 1932, **104**, 734–736.)—The point at which crystals begin to form in volume-volume concentrations of "prestone" (a brand of ethylene glycol anti-freezing material) is taken as the freezing-point, and recorded against the n_D^{20}, which is the most convenient and rapid reading to take.

Parts of water	9	8	7	6	5	4	3	2	1	0
Parts of "Prestone"	1	2	3	4	5	6	7	8	9	10
$n_D^{20\,°C}$	1·3437	1·3540	1·3642	1·3745	1·3845	1·3943	1·4038	1·4130	1·4220	1·4298
Freezing-point, °F.	27	17	4	−14	−34	−56				

D. G. H.

Detection and Estimation of Medullated Fibre in New Zealand Romney Fleeces. B. L. Elphick. (*J. Text. Inst.*, 1932, **23**, 367T.)—The various genetic, nutritional and climatic conditions governing the production of medullated fibre (*i.e.* persistent hairy fibre, as distinct from kemp) are one by one being brought under investigation, and a reduction in medullation should eventually be achieved. A test for medullation, which can be utilised in the laboratory for individual fibres or on a farm by unskilled hands for a staple, is the benzene test. This test depends on the fact that the refractive indices of wool keratin and benzene are very similar, so that air-filled medullae are easily detected by immersing the staples in benzene.

The test is as follows:—The staple is scoured in petroleum spirit, to remove grease and dirt, and dried off. It is then teased with the fingers into a thin uniform layer and laid in a shallow, black tray of enamelled iron containing benzene. A glass plate is carefully lowered on to the wool so as to exclude all extraneous air bubbles. The staple is then examined by diffused daylight, when not only medullated fibres, but also their distribution in the staple, will be visible. Occasionally two abnormal conditions are met with in Romney wools which affect the application of the test: (i) a condition of the pure wool fibre which gives it a pale smoky appearance; (ii) an apparent infilling of the medulla after about a year's storage of certain wool samples. The degree of medullation is best expressed as the proportion by volume of medulla to the total volume of the fibre. This requires the following dimensions to be separately evaluated and integrated into a single value: (*a*) mean diameter of medulla, (*b*) mean diameter of fibre, (*c*) proportion of total length of medullated fibre. The distribution of medullated fibre over a fleece has been found to spread from the britch to flank, rib, back, shoulder, and wither, the latter being least likely to be medullated. In sampling a fleece for breeders testing their own sheep, the flank is considered the critical area, but for research work, britch, side and shoulder wools must be sampled according to the standard procedure described. R. F. I.

Acidity of Vegetable-tanned Leather. W. R. Atkin and F. C. Thompson. (*J. Inter. Soc. Leather Trades Chem.*, 1932, **16**, 591.)—The authors summarise recent work on the determination of the acidity of vegetable-tanned leather by the physical methods initiated by Innes in 1928, and elaborated by Atkin and Thompson in 1929. These two methods have been tried separately or comparatively by Pollak, Kubelka, Merrill, and Bennett. The review consists in meeting criticisms of the Atkin–Thompson method, re-stating the contention that fully-tanned leather is a gel and contains free amino groups, and in condemning the Innes method as giving misleading results. The essential point of difference between the two methods is that in the Innes method the leathers are extracted with water, whilst in the Atkin–Thompson method 0·1 *N* potassium chloride solution is used, and is said to have the effect of equalising the concentration of the acid inside and outside the gel.

Abstractor's Note.—The relative merits of the two methods mentioned are at present being experimentally compared by the Committee on the Analysis of Vegetable-tanned Leather of the British Section of the I.S.L.T.C., with a view to deciding which is the more accurate and convenient. At present both are official methods of the Society. R. F. I.

Inorganic Analysis

Titration Method for the Determination of Water. R. P. Bell. (*J. Chem. Soc.*, 1932, 2903–2905.)—Water reacts with α-naphthoxy-dichlorophosphine, as follows:—$C_{10}H_7O.PCl_2+2H_2O \longrightarrow C_{10}H_7.O.P(OH)_2+2HCl$, and the acid may be removed in a current of air and titrated, the method being more rapid than the similar reaction proposed by Lindner (*Z. anal. Chem.*, 1925, **66**, 305). The reagent is prepared from α-naphthol and phosphorus trichloride (Kunz, *Ber.*, 1894, **27**,

2560), and, after distillation in a vacuum and removal of excess of phosphorus trichloride in a current of dry air at 100° C., it is obtained as a colourless non-fuming liquid, b.pt. 180 ± 1° C. The reagent (1 c.c.) is dissolved in 5 c.c. of benzene, or preferably bromo-benzene (to accelerate the reaction), and dry air is bubbled through the mixture and into a U-tube containing water at the rate of 50 to 100 c.c. per minute. When a titration value of about 0·05 c.c. of 0·1 *N* sodium hydroxide per hour is obtained, the sample is added, the mixture is shaken, and, after 30 minutes, the current of air is again passed at the same rate. Titrations are made at intervals until the value again drops to 0·05 c.c. per hour, and the correction is calculated from the data obtained in the control experiment. The maximum recorded error with 25 to 62 mgrms. of added water is 0·3 mgrm. Examples are given of the use of the method for the determination of water (of the order of 4 mgrms.) in benzene, and of water-vapour in air. In the former case the result obtained for the solubility of water in benzene was between the two most reliable published results, and in the latter three similar experiments (in which first a known volume of sample and, secondly, dry air, were passed through the solution of reagent) gave 9·80, 10·80 and 10·03 mgrms. of water per 500 c.c.

J. G.

Notes on the Analytical Behaviour of Gallium. E. S. von Bergkampf. (*Z. anal. Chem.*, 1932, **90**, 333–335.)—(1) *Selective solution of aluminium from aluminium-gallium alloy.*—In accordance with the electro-positive nature of gallium to aluminium, the latter may be dissolved selectively from an alloy containing a few units per cent. of gallium by means of dilute sulphuric acid, the gallium remaining as the liquid metal. Gallium itself dissolves very slowly in the absence of metals electro-positive to it.

(ii) *Limits of p_H for the precipitation of gallium hydroxide and aluminium hydroxide.*—The following values were obtained with the aid of the quinhydrone and hydrogen electrodes, 0·1 *N* solutions being used:

p_H Values at the beginning of precipitation

	Acid	Alkaline
$Ga(OH)_3$	3·4	9·7
$Al(OH)_3$	4·14	10·4

(iii) *Precipitation by Cupferron.*—Gallium may be precipitated quantitatively by cupferron from a solution containing tartrate and not more than 1·5 per cent. by volume of concentrated sulphuric acid; the upper limit of acidity is thus close to that for the precipitation of aluminium by cupferron. Iron and titanium may be separated from gallium by precipitation from a solution of higher acidity containing, *e.g.* 5 per cent. by volume of concentrated sulphuric acid. S. G. C.

Preparation and Properties of Thallous Thiocarbonate. Picon. (*Compt. rend.*, 1932, **195**, 1274–1276.)—Interaction of thallous sulphide and carbon disulphide in a faintly alkaline medium yields a black precipitate, which soon changes to a vermilion colour (thallous thiocarbonate, Tl_2CS_3). When washed with boiling water and dried in a vacuum in presence of phosphoric anhydride, the cold salt is perfectly stable, but complete decomposition into thallous sulphide and carbon disulphide occurs *in vacuo* at 100° C. The compound is stable towards

water and alkalis at the ordinary temperature, and is insoluble in the ordinary organic solvents. Cold inorganic acids decompose it, with formation of the corresponding thallous salts, but aqueous solutions of organic acids attack it only when heated. Its solubility in water is so slight that its formation may be used for detecting 1 part of thallium in 50,000 parts of solution. To 1 or 2 c.c. of the solution are added a few drops of carbon disulphide, and then ammonia solution until no further precipitation occurs. Sufficient excess of ammonium hydrosulphide to produce a yellow colour is added, and the liquid is heated very gently until the carbon disulphide begins to boil. If thallium in the thallous state is present, the ammonia added will give no precipitate, but subsequently the black sulphide and the vermilion thiocarbonate are formed in turn. If tervalent thallium is present, the ammonia yields a black precipitate, and later the vermilion salt appears. T. H. P.

Gravimetric Determination of Cobalt by means of Dinitrosoresorcinol. O. Tomiček and K. Komárek. (*Z. anal. Chem.*, 1932, **91**, 90–105.)—The method of precipitation of cobalt by means of dinitrosoresorcinol, proposed by W. R. Orndorff and M. L. Nichols (*J. Amer. Chem. Soc.*, 1923, **45**, 1439), has been critically examined. It was found that, provided the original directions were strictly adhered to, satisfactory results could be obtained. The process is, however, subject to compensating errors, since the precipitation of cobalt is not quite complete, and some adsorption of the excess of reagent and of salts present in the solution occurs on the precipitate. Attempts made to improve the process were unsuccessful. S. G. C.

Determination of Aluminium Oxide in Aluminium Alloys. W. Ehrenberg. (*Z. anal. Chem.*, 1932, **91**, 1–5.)—The drillings or, preferably, sawings, are mixed and rubbed as fine as possible in a mortar, and 3 grms. are weighed into a 1000-c.c. beaker. About 70 grms. of pure cupric chloride are added, followed by 100 c.c. of water. When foaming has subsided, the liquid is boiled for a few minutes during agitation until the precipitated copper has dissolved. After a short period of settling, the boiling-hot liquid is poured through a 12·5-cm. funnel containing a pad of filter pulp (finely-divided silicon running through the filter is disregarded). The filter is washed with hot water until the dark brown coloration has been removed, then with hot dilute nitric acid (about 1:5) until the washings fail to react with ammonia. The acid is displaced with water, the washed residue is ignited in a tared platinum dish, and the silicon is removed by evaporation with nitric and hydrofluoric acids. The ignited residue from the last treatment is weighed as Al_2O_3. Several determinations can be made within 3 hours by one operator; the results given are satisfactory. The above solution process is also recommended for other determinations in rapid work. The usual methods for the determination of oxide in aluminium require special apparatus and, according to the author, yield results which must be regarded with suspicion. W. R. S.

Colour Reaction for Nitrites. A. Castiglioni. (*Z. anal. Chem.*, 1932, **90**, 427–429.)—The test is based on the reaction of nitrous acid with phenols or their derivatives containing a free phenolic group, in particular with pyrocatechol or

sodium 2, 6 diiodo-*p*-phenolsulphonate ("sozojodol"). When heated with a few mgrms. of solid reagent, the nitrite solution (1 c.c.) assumes a cherry-red coloration; the reaction detects one part of sodium nitrite in 100,000 of solution. With pyrocatechol the reaction is ten times more sensitive: the liquid should be made alkaline with sodium hydroxide after having been heated with the solid reagent. A wine-red colour is obtained. The reaction is specific, as it is not given by nitrates, chlorates, bromates, iodates, or chromates. W. R. S.

Hydrated Dicalcium Aluminate. H. Lafuma. (*Compt. rend.*, 1932, **195**, 1276–1278.)—The existence of this compound and its formation during the hydration of aluminous cements, previously noted by the author (Thesis, Paris, 1925), have been contested by some and confirmed by others. Further experiments show that it is undoubtedly formed in the hydration of *ciment fondu*. T. H. P.

Determination of Fluorine by Precipitation as Triphenyl Tin Fluoride. N. Allen and N. H. Furman. (*J. Amer. Chem. Soc.*, 1932, **54**, 4625–4631.)—Krause and Becker (*Ber.*, 1920, **53**, 183) found that the addition of triphenyl tin chloride to a solution of a fluoride resulted in the precipitation of very difficultly soluble triphenyl tin fluoride. This reaction has been studied, and the following process is proposed: To the fluoride solution sufficient ethyl alcohol (95 per cent.) is added to comprise 60 to 70 per cent. of the final volume, and the solution is heated to boiling. About twice the calculated amount of boiling aqueous triphenyl tin chloride solution (containing 0·02 grm. per c.c.), diluted with an equal volume of alcohol, is slowly added to the hot fluoride solution, with rapid stirring; the whole is then boiled, allowed to cool down somewhat, the stirring being continued, and then set aside overnight. If the quantity of fluorine is large, the precipitate forms in large white crystals within about one minute of the addition of the reagent, but with small amounts it does not appear until the solution has cooled to room temperature. On the following day the liquid is cooled in ice for about 1 hour (with the larger amounts of fluoride this step may be omitted). The precipitate is filtered off on a sintered glass crucible, washed with about 50 c.c. of cold ethyl alcohol saturated with triphenyl tin fluoride, and is then dried for 30 minutes at 110° C., and weighed; it contains 5·153 per cent. of fluorine. Good results are cited of determinations of amounts of fluorine from 47 mgrms. down to 0·05 mgrm.; with the smaller quantities the volume of solution at the precipitation stage was 15 c.c. The method is stated to be more particularly suitable for small quantities of fluorine, and does not lend itself well to quantities greater than about 0·04 grm. owing to the considerable volume of reagent solution required and the bulk of the precipitate produced. The p_H of the fluoride solution should be between 7 and 9; if too acid, some fluorine is liable to be lost on heating the solution, and, if too alkaline, triphenyl tin hydroxide will be precipitated with the fluoride. If present in only moderate quantity, nitrate, chloride, bromide, iodide, and sulphate are without interference; but carbonate should be removed by neutralising the solution with acid and boiling out the carbon dioxide. Silicic acid and phosphate must be eliminated by prior treatment of the fluoride solution by the method of Berzelius. The method has been applied with some success to the analysis of fluorspar, and further applications are under investigation. S. G. C.

Separation of Selenocyanate from Halides. G. Spacu and V. Armeanu. (*Z. anal. Chem.*, 1932, **90**, 429–432.)—The solution is treated with an equal volume of reagent, made by dissolving 10 grms. of crystallised nickel nitrate in 35 c.c. of water and adding 10 c.c. of pyridine. The liquid is stirred and cooled, and the sky-blue precipitate $[NiPy_4] (SeCN)_2$ is filtered off. The filtrate is acidified with nitric acid and the halides are precipitated with silver nitrate. W. R. S.

Volumetric Determination of Free Sulphur. A. Castiglioni. (*Z. anal. Chem.*, 1932, **91**, 32–33.)—The acetone extract (from rubber, golden sulphide, etc.) is boiled with excess of potassium cyanide for half an hour under reflux; the solution is evaporated on the water-bath, and the dry residue is dissolved in 100 c.c. of water and transferred to a 200 c.c. flask. The solution is agitated with 10 c.c. of 20 per cent. formaldehyde, acidified with 5 c.c. of 30 per cent. nitric acid, and made up to 200 c.c. Portions of 20 c.c. are treated with 5 to 6 drops of 10 per cent. ferric nitrate solution, and titrated with 0·05 *N* silver nitrate solution until the red colour just disappears. W. R. S.

Microchemical

Micro Vapour Density Determination. Part I. Determination of Molecular Weight. J. B. Niederl and W. J. Saschek. (*Mikrochem.*, 1932, **11**, 236–250.)—The authors' previous method (*Mikrochem.*, 1929, **7**, 377, and *Z. anal. Chem.*, 1929, **77**, 170) is improved. The method consists in vapourising a weighed sample in a flask, and weighing the mercury displaced. The weight of mercury displaced by the vapour of a 5-mgrm. sample of a substance of 240 molecular weight is approximately 8·5 grms., so that an ordinary analytical balance may be used. The apparatus consists of a spherical or pear-shaped flask of 7 to 10 c.c. capacity. A tube, of about 8 cm. long and 0·5 to 0·7 cm. bore, is fused into the upper part of the flask to serve as a handle and as a holder for the thermometer. Near the bottom of the flask is a ground-glass neck (1 cm. long, 6 mm. bore), into which the hollow stopper (1·5 cm. long, 5·2 to 5·4 mm. bore) of a capillary (2 mm. bore) delivery tube fits. Just beyond the stopper the outlet tube is bent vertically upwards for 6 cm., and then horizontally for 3 cm., so that its orifice extends beyond the heating bath. The receiver may be a small graduated test-tube or a centrifuge tube of 7 to 10 c.c. capacity. The correction for the heat expansion of the flask and of the mercury is determined empirically by carrying out a determination with the apparatus filled with mercury. The capillary outlet tube is filled with mercury by means of a pump similar to a fountain-pen filler, with a narrow capillary outlet, which will fit inside the 2 mm. capillary. The weight of mercury, divided by the temperature interval, gives the expansion correction in grms. per 1° C. for the apparatus. The pressure of the vapour is made up of the barometric reading corrected for temperature, and the pressure of the mercury column in the capillary outlet tube (reduced to 0° C.); the correction for capillary depression (8 mm.), and the vapour pressure of mercury at the final temperature must be subtracted. *Method.*—Samples of 5 to 10 mgrms. are used and weighed into small capillary pipettes made of 1 mm. capillaries drawn out to hair capillaries at each end. These may be filled in the Pregl method by sealing one end and gently warming the bulb, and then dipping the tip in the liquid. When filled the

tubes must be centrifuged, the other end then sealed, and the tubes are then weighed on a micro-balance, having previously been weighed empty. The tip free from liquid is then broken, and the tube is placed in the bulb, which is immediately filled with mercury, the outlet tube being fitted after greasing the stopper, which should be wired to prevent loosening. The fitted apparatus is placed in a cold bath (for substances boiling below 100° C. water is used) to obtain a constant temperature. The bath is then slowly heated to boiling, and kept so for about 15 minutes, after which the final temperature is noted. The mercury receiver is then removed and weighed, and the pressure-difference of the mercury in the flask and capillary tube is measured. Repeated determinations can be made on a single sample by dipping the delivery tube into mercury before cooling, in order to refill the apparatus. The apparatus may be used simultaneously for determining the b.pt., which is taken as the temperature of the most rapid flow of mercury when heating, or most rapid rush of air bubbles into the apparatus on cooling. Results with liquids of low b.pt. differed from the theoretical by about 1 to 2 per cent.; with liquids of high b.pt. by 2 to 5 per cent. J. W. B.

Micro Vapour Density Determination. Part II. Determination of Boiling-points. J. B. Niederl and I. B. Routh. (*Mikrochem.*, 1932, **11**, 251–273.)—The apparatus described in Part I (above) is simplified for boiling-point determinations. The diameter of the flask is reduced, and the side-arm is sealed to the flask instead of being attached with a ground-glass joint; the side-arm diameter is 3 mm. and the angle between the arm and the vertical axis of the flask is about 60°. The side-arm is attached by means of a ground-glass joint or rubber tubing to a glass tube (3 mm. in diameter), bent so that the main portion is horizontal. The progress of mercury along this tube can be watched more accurately if it is attached to a scale. The tube containing the thermometer should contain enough mercury to cover the bulb and ensure proper contact with the flask wall. The sample is introduced without air bubbles by heating a small piece of porous tile and immersing it while warm in the liquid. The pores of the tile are completely filled with the liquid, and it may be dropped down the side-arm of the bulb, the apparatus filled with mercury, and the heating begun. By repeatedly heating and cooling, a large number of readings of the b.pt. may be made on the same sample. The readings are taken, both on heating and on cooling, by noting the temperature of formation and disappearance of the gas space by the rapid advance of mercury in the horizontal tube, and by the constancy of the temperature at the point of complete vaporisation on condensation. The pressure corrections, as used in the determination of molecular weight (*cf.* Part I), must be made, and the temperature correction is calculated from the pressure by the method in the International Critical Tables for large differences, or Kahlbaum (*Ber.*, **1886**, **19**, 101), or Houben's (*Methoden der organischen Chemie*, Vol. I, Leipzig, 1925) simpler rules are sufficiently accurate for small differences in pressure. Good results were obtained with a number of liquids. Solids may also be used in this apparatus. Approximate molecular-weight determinations may be made by measuring the volume of mercury displaced from the length of mercury in the horizontal tube. J. W. B.

New Method of Carrying out "Spot" Tests. J. Winkelmann. (*Mikrochem.*, 1932, **12**, 119–128.)—A new medium of gelatin or glycerin jelly is proposed for carrying out "spot" tests. In this method permanent preparations can be mounted easily and give a useful record of the tests. This is an advantage over ordinary "spot" methods on a white tile or in a test tube, and is also better than the use of impregnated filter-paper on which the colour developed is seldom permanent. *Preparation of Medium.*—Ten grms. of gelatin are washed, with constant changing of water, for 48 hours in cold distilled water, and then dried with filter-paper or cloth, and melted over a water-bath; this gives an approximately 20 per cent. solution. To this 30 c.c. of glycerin are added, and the mixture is diluted to 100 c.c., heated to 100° C. with a crystal of thymol, and filtered hot into bottles with dropping pipettes. In summer it is recommended that 0·5 per cent. of agar-agar be added. Ordinary glycerin jelly may be used instead of the prepared mixture. When glycerin and gelatin give precipitates with the reagents the medium cannot be used. Gelatin is dissolved by strong acids, alkalis, and concentrated solutions of cyanides and thiocyanates and related complex ions, but usually the amount of these reagents used is too small to affect the gelatin. *Method I.*—From 6 to 10 drops of the gelatin medium, warmed if necessary, are mixed with 1 or 2 drops of the reagent on a slide, which should be 3·5 to 4·0 cm. wide by 7·0 to 7·6 cm. long. For every test several slides should be covered with mixtures of reagent and medium containing varying percentages of the reagent, in order to find out the best concentration of reagent, and (if necessary) of acid or alkali, for the test in question. A micro-drop, of 1 to 3 mm. diameter, of the test solution is placed on the cooled medium on the slide with a platinum or glass needle. A large number of drops may be placed on the same slide, and both a blank and a standard test (from a solution containing a known amount of the test element) must be carried out simultaneously. Characteristic crystals are formed and colour changes take place as clearly as in the other methods of carrying out the "spot" tests. *Method II.*—The slide is covered with the mixture of medium and reagent as before, but a drop of the test solution is evaporated to complete dryness on another slide, and the crystal dust is scraped on to the gelatin mixture with a fine platinum wire or glass rod. In this way the tests may be made extremely sensitive. *Other Methods.*—Where two reagents are used, one may be mixed with the medium and the other placed near the test drop, so that they gradually run together. Tests may be carried out by evaporating the test solution to dryness on a slide, and then applying the mixture of gelatin medium and reagent. The methods I and II are the most general.

Permanent preparations.—It is best to use only 1 or 2 drops of gelatin medium, so that it does not spread over the whole slide. After the reaction is complete the gelatin preparation is washed to remove excess of reagent, hardened with formalin and dried. It is then covered with a coverslip moistened with Canada balsam and allowed to set. Glycerin jelly preparations may be covered with a coverslip on which is a drop of glycerin jelly; the preparation should then be very carefully warmed, the excess of glycerin jelly removed with filter-paper, and, after the edges round the coverslip have been cleaned with formalin, the coverslip is sealed with gold size.

J. W. B.

Temperatures of Sublimation of Twelve Amino-Acids. J. W. Brown. (*Trans. Roy. Soc. Canada*, 3rd series, 1932, **26**, 173–175.)—The temperature of sublimation and crystalline appearance of the sublimate may be used as a rapid method of identifying small quantities of some amino-acids. In the determinations described, Eder's method (ANALYST, 1913, **38**, 426) of micro-sublimation *in vacuo* was used. The cooling distance was 4 mm., and the pressure 13 mm., 0·1 mgrm. or less of material was used, and the sublimate was collected on a coverslip. The temperature of sublimation was taken as that at which an appreciable sublimate was obtained in 10 minutes under the conditions of the experiment.

Sublimation temperatures of twelve amino-acids

	Subl. temp. °C.	M.pt. °C.		Subl. temp. °C.	M.pt. °C.
l-Proline	130–135	220	*iso*-Leucine ..	168–170	280
l-Leucine.. ..	145–148	293–5	Glutamic acid ..	170–175	197–8
iso-Valine ..	150–151	315	Tryptophane ..	185–190	289
l-Phenylalanine	150–155	283	Oxy-proline ..	185–190	270
d-Alanine ..	160–165	297	*l*-Serine	186–190	228
Glycine	160–175	225–30	*l*-Tyrosine ..	250–256	314–8

The following do not sublime: *d*-arginine; *d*-aspartic acid and histidine.

l-Proline, glycine, oxy-proline, serine and tyrosine give crystalline sublimates which are easily recognised and distinguished. *l*-Leucine, *iso*-valine, *l*-phenylalanine, *d*-alanine, and *iso*-leucine give good crystalline sublimates, but of similar appearance. The tryptophane sublimate is a cloudy decomposition product, and glutamic acid gives only droplets. Further tests, such as solubility and simple colour tests, may be applied to the sublimates. Phenylalanine may be distinguished from leucine by the formation of a red colour with fuming nitric acid. The melting-points of the sublimates may be determined under the microscope by using an electrically-heated stage. Photomicrographs are given of some of the sublimates. J. W. B.

Microchemical Identification of Caffeine. H. J. Sandrus and M. L. Willard. (*Mikrochem.*, 1932, **12**, 137–142.)—Twenty-three residues, obtained by evaporating mixed solutions of caffeine and metallic salts in the presence of an acid, are described; the most characteristic and best crystallised precipitates were obtained with aluminium nitrate, strontium nitrate, silver nitrate, platinous chloride, mercuric nitrate, thallous nitrate, bismuth nitrate, and barium nitrate. These, upon further examination and analysis of the complex, might be used to identify caffeine. Palladous chloride caused the precipitation of caffeine, almost instantly, as a light yellow powder, appearing, under the microscope, as needle-shaped crystals often arranged in star-shaped groups. In the presence of acid no precipitate was given by caffeine with calcium nitrate, manganous nitrate or zinc chloride. J. W. B.

Microchemical Identification of (*Lunasia*) Alkaloids. F. Amelink. (*Pharm. Weekblad*, 1932, **69**, 1390–1396.)—(*A*) Lunasine, $C_{16}H_{21}N_2O_5$, and (*B*) lunacrine, $C_{16}H_{20}O_3$, occur in *Lunasia amara* (*blanco*) *var. costulata* (*Hoch*).

A crystallises from chloroform in small colourless needles (m.pt. 188 to 189° C.), which are readily soluble in alcohols, and also in water, to give a fluorescent solution, [α] —38°, but are almost insoluble in ether, benzene or petroleum spirit. *B* crystallises in long 8-sided needles (m.pt. 115 to 116° C.), and is readily soluble in alcohol, chloroform or benzene, slightly soluble in warm water or ether, and sparingly soluble in cold water or petroleum spirit. Solutions in water react as a weak base, ([α] —38°), and have a blue fluorescence in ultra-violet light, although in a dark room the powdered solid substance appears yellow. The respective reactions with strong sulphuric acid are light yellow and colourless; with Fröhde's reagent, blue-green and purple-blue; with Erdmann's reagent, pale-yellow and yellow-green; with Marquis' reagent, orange-yellow with a green fluorescence, and dirty yellow-green turning to red on warming; and with Wasicky's reagent, yellow and orange-yellow. For the following reactions the alkaloids should be evaporated with dilute hydrochloric acid, 0·5 per cent. solutions of the residue in water and in 0·05 *N* hydrochloric acid being then examined by the drop technique under the microscope. *Platinic chloride* (in the presence or absence of sodium iodide).—(*A*) Light yellow precipitates with both solutions, consisting of thin double-refracting plates, which appear in solutions of 0·1 per cent. strength. (*B*) A yellow granular precipitate melting at a low temperature to form droplets which crystallise (particularly from the acid solution) in star-shaped groups of fine double-refracting needles. *Gold trichloride* (in the presence or absence of sodium bromide).—(*A* and *B*) A yellow precipitate of weakly double-refracting, fine, hair-like needles is obtained in 0·1 per cent. solutions. *Mercuric chloride.*—(*A*) In both solutions a white precipitate, forming droplets if warmed, is produced in solutions stronger than 0·1 per cent. (*B*) Needles and prisms are formed in acid solution (sensitiveness 0·1 per cent.), but the reaction is negative in neutral solution. *Potassium ferrocyanide.*—(*A*) Droplets are formed in neutral solution, and a white uncrystallisable precipitate is obtained from the acid solution. (*B*) A white uncrystallisable precipitate is obtained from acid solutions, and fine *d*-rotatory prisms from neutral solutions. *Potassium ferricyanide.*—(*A*) Star-shaped groups of needles are slowly deposited in both cases from cold solutions stronger than 0·2 per cent. (*B*) Weakly double-refracting needles are obtained from cold acid 0·1 per cent. solutions. *Dragendorff's reagent.*—(*A* and *B*) Droplets (brown in the case of *B*) are obtained in both cases on warming, and from both solutions. *Potassium hydroxide.*—(*A*) Only droplets are obtained. (*B*) Star-shaped groups of thin, weakly double-refracting prisms are obtained from 0·1 per cent. solutions. *Picrolonic acid.*—(*A*) Double-refracting needles are deposited from neutral solutions. (*B*) Droplets only are obtained. The above crystal forms are illustrated in a number of cases. In addition, sodium bromide and iodide and ammonium sulphate also give needle-shaped crystals which, however, cannot be used to distinguish *A* from *B*; and cobalt nitrate produces characteristic brown crystals with *A* only.

J. G.

Reviews.

THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS. SOME REMINISCENCES OF ITS FIRST FIFTY YEARS, by BERNARD DYER, D.Sc., F.I.C., and A REVIEW OF ITS ACTIVITIES, by C. AINSWORTH MITCHELL, M.A., D.Sc., F.I.C., Editor of THE ANALYST. Indexed by M. B. ELLIOTT, M.B.E. Published for the Society by W. Heffer & Sons Ltd., Cambridge. 1932. Price 12s. 6d. (Members, 7s. 6d.).

"It is thus," says Gibbon, "that the experience of history exalts and enlarges the horizon of our intellectual view. In a composition of some days, in a perusal of some hours, six hundred years have passed away, and the duration of a life or reign is contracted to a fleeting moment; . . . and our immortal reason survives and disdains the sixty phantoms of kings, who have passed before our eyes and faintly dwell on our remembrance."

The Kings in this book—the successive Presidents of the Society—are not, like the successive Emperors in Gibbon's picture, seen plotting and scheming, "to obtain and hold," through crime and intrigue, "the sceptre of dominion"; we look upon them, as Dr. Dyer passes them in array before us, not with disdain, but rather with admiration and gratitude; they will dwell in our remembrance, thanks to Dr. Dyer's happy power of description, not faintly, but vividly and enduringly; and after our "perusal of some hours," we shall indeed feel that our intellectual view of the progress of analytical chemistry has been exalted and its horizon enlarged.

We start with the foundation of the Society as the result of a meeting in 1874, attended by some 27 members, and learn that the first general meeting was held in February, 1875, and that at the first annual meeting in January, 1876, there was a total membership of 70. We follow the fortunes of the Society, constantly increasing in numbers and influence, through the time of its incorporation in 1906 under its present name, till its Jubilee year in 1925, when its membership was close on 500.

We see the modest beginning of its publishing activities, in a corner of the *Chemical News*; very soon, however, came the establishment of THE ANALYST, which, controlled by a Committee and edited by an official of the Society, was held in trust for the Society under the proprietorship of two of its members, Wigner and Muter, as the Society had no corporate existence. After a year, it was made over absolutely, for financial reasons, to these two, the Society making a definite contribution; and only in 1891 was it again taken over by the Society, and held in trust by three members. This arrangement held till 1906, when the Society was incorporated, and the ANALYST was transferred from the Trustees to the Society.

We learn how, from the very beginning, the Society has steadily pressed for the institution of standard definitions of foodstuffs. One of its earliest acts, in its

first year, was to lay down and publish suggested standards for milk, butter, tea, cocoa, and vinegar; and it has continued, down to the present time, to urge this matter upon Government authorities.

A high standard, both of qualification and of ethical practice, has also been, from the first, the policy of the Society. Severe disciplinary action was taken, very early, and again in later years, against members who offended against the standard of ethics; and in 1890 the Society memorialised the Local Government Board in favour of higher qualifications for those aspiring to the position of Public Analysts.

Here and there Dr. Dyer treats us to little essays, all compact and all illuminating, which add much to the charm and to the usefulness of the book—the condition of food analysis in 1875—the relations of the Society to the Government Laboratory—those of the Society to the Institute of Chemistry—and, in lighter mood, the Dinners of the Society—these alone, were there nothing else, would amply repay the reader.

Many of our predecessors were men of strong convictions—possibly of strong prejudices—and sometimes of uncertain and hasty tempers; and the deliberations of Council, and indeed of the Society, seem not always to have been model exhibitions of suavity and of polite deference to the opinions of others. Dr. Dyer tells us of these things as well as of those more agreeable; but he touches on them very gently and impartially, and both here and in his sketches of the personality of some of the presidents and other distinguished members of the Society, his kindliness to a fault, his recognition of the merits of "the other side," his near approach to the attitude of "tout savoir, c'est tout pardonner," not only add charm to his descriptions, but also throw their light upon the author himself, whom we all regard with affection, and rejoice to have still amongst us, well towards the end of the first decade of the "Second Fifty Years."

If I say but little of Dr. Mitchell's portion of the book, it is because from its nature there is but little to say about it—all would perhaps be contained in the statement that it is what we might have expected from Dr. Mitchell. It is really a classified abstract of the proceedings of the Society during the fifty years. It is divided into decades, and in each decade separate substances are separately treated. The labour of doing this must have been immense, and no one could have done it better than Dr. Mitchell, who seems to have an instinctive sense of the relative importance of things, and of the amount of space necessary to give the right amount of information regarding each. With the help of Miss Elliott's very comprehensive index, one can trace any substance, analytical methods suggested or used for its detection or determination, and legal cases involving it, through the half-century, in a very short time, and for this purpose the work will be of very great use.

Every member of the Society, and every budding or prospective Public Analyst, must use this book, and will derive from it not only profit but enjoyment. And all outside the Society, who have any sort of connection with, or interest in, analytical chemistry, should purchase and read it, and will have no sort of regret at having done so.

J. T. DUNN

VITAMINS: A SURVEY OF PRESENT KNOWLEDGE. Compiled by a Committee appointed jointly by the Lister Institute and Medical Research Council. Pp. 332 + 12 plates. London: His Majesty's Stationery Office. 1932. Price 6s. 6d.

For some years food chemists in general, and food analysts in particular, have had an uneasy feeling that their analytical procedure was not altogether abreast of the times. All of us have known that the nineteenth-century analysis of food into its primary constituents, fat, protein, carbohydrates, minerals, and water, could not reveal its true food value, and that there was rapidly accumulating knowledge of "accessory food factors" that defied all known means of chemical analysis, and whose presence or absence made the difference between a food that was perfect and one that was literally lethal. We were apt to sit back, rather despondently, hoping for such advances in biochemistry as would make it possible for the analyst in public, industrial, or private practice, to give a particular food to an animal on a particular diet, and to say, within a week at most, that this food contained x parts (by volume, by weight, or by unit) of vitamin ψ—for by that time we should be well into the Greek alphabet.

It must be admitted that the biochemists, if this was expected of them, have failed us grievously. Each of their advances in the technique of animal assay seems merely to have had the result of making the procedure more complicated and more expensive than had previously been thought necessary and justifiable. A proposal to test an unknown substance in three different doses on three pairs of animals makes the bio-assayist, who to-day is at least as much statistician as physiologist, either snort with anger, or laugh with derision, but to have to carry out the test on a number of animals sufficient to placate the bio-assayist's sense of propriety would cause the chief of an industrial laboratory to gnash his teeth and throw in his hand.

Things being as they are, the food chemist will turn with some expectation to the Report compiled by the Accessory Food Factors Committee, and published by the Medical Research Council, who, according to the regular practice, place the responsibility for all the views and opinions given in the Report on the shoulders of its compilers. The Report is the third that the Medical Research Council have published on the subject, but this latest version is much more than a mere revision. It has been completely re-arranged and re-written, and in its compilation most of the leading British experts in the field have taken part. It represents a complete, comprehensive, fair and accurate summary of the state of vitamin knowledge at the end of 1931, and it is of some interest to note that the Medical Research Council do not propose to "do it again." They say, and in my opinion rightly, that the seeker after further knowledge can get all he wants from the admirable abstracts and reviews published in their quarterly periodical *Nutrition Abstracts and Reviews.* The implication, that the study of vitamins is now an established and recognised branch of biochemistry, physiology, or chemistry, is a true one, and one that literally marks an epoch.

It is, therefore, by an unfortunate whimsie of fate—at any rate from the analyst's point of view—that just in 1932 some of the most important advances

in the non-biological assay of vitamins should have been made. Certainly, it would be difficult to deduce from the Medical Research Council's Report that vitamin *D* would in one year's time be commercially available as a pure crystalline substance, and that vitamin *A* could be measured probably as accurately with a spectroscope as by tests on rats. The isolation of vitamin B_1 as a nearly pure crystalline base is duly chronicled in the Report, but the probability that vitamin *C* and hexuronic acid are one and the same thing was not foreseen, even by the experts that took part in making this invaluable compilation. That the study of vitamins B_2 and *E* should not have brought us anywhere near the possibility of chemical or physical estimation is to be attributed to the fact that the one has been recognised as a specific entity only for about 2 years, and that the other, of all known vitamins, involves in its investigation the most expensive and laborious technique.

Yet, when even the present relatively crude state of our knowledge is compared with that chronicled by the Medical Research Council's previous Report on vitamins, it must be realised that the advances made have been significant and profound. It is almost certainly not an over-bold prophecy to forecast that the lapse of a further eight years will have put us in a position to make at any rate approximate assays of the more important vitamins in any well-equipped chemical laboratory. It is possible to state quite briefly how far we have to date proceeded in this direction.

Vitamin *A* depends for its standardisation fundamentally on accurate biological assay, but the best workers in this field do not claim a precision of more than ± 20 per cent., when using as large a number of animals as can reasonably be expected even in a research laboratory. Results consistent with those of the most accurate animal assay can be obtained by measuring the intensity of absorption of the ultra-violet band of wave-length $328 m\mu$. Moreover, provided certain precautions are taken, results very close to these can also be obtained by means of the antimony trichloride colour-test, and these results do not differ materially whether the depth of colour produced is measured in the Lovibond tintometer, or by means of the two absorption bands at 580 and $617 m\mu$ that give rise to the blue colour. Any of these physical methods will give results practically identical with those of biological assay when they are carried out on very rich concentrates of vitamin *A*; the further we depart from the "pure" vitamin, the more difficult does it become to achieve this degree of accuracy. Nevertheless, it is quite possible to take cod-liver oil itself—or even butter-fat, if the vitamin is separated from this in the unsaponifiable matter—and to compare it quantitatively either with another cod-liver oil, or with a rich vitamin *A* concentrate, by means of the spectroscope alone; a further test with antimony trichloride, using the tintometer or spectroscope, would either confirm this estimate, or allow a weighted mean to be calculated.

In the direction of vitamin *D* assay advance has been in some respects greater, and in some respects less, than for vitamin *A*. It is possible to assess the purity of the vitamin itself by ordinary physical and physico-chemical measurements. By that same token it is possible from very rich specimens of irradiated ergosterol to separate serially the unchanged ergosterol, the other inactive substances, and

the pure crystalline vitamin *D*, and therefore to assign a specific biological activity to the irradiated material by physical and physico-chemical tests alone. The process is, however, quite inapplicable to ordinary "natural" sources of vitamin *D* —even to such rich ones as the most potent cod-liver oils, which may contain as much as 0·00125 per cent. of the vitamin.

When it is finally confirmed that hexuronic acid and vitamin *C* are identical, our fairly precise knowledge of the physical and physico-chemical constants of the one will clearly be applicable to the other, but we have not yet reached that position; nor, indeed, can we say to what extent hexuronic acid can be chemically or physically identified in those natural sources from which it has actually been isolated, such as the adrenal gland, green leaves, and citrous fruit juice. The position is much the same with vitamin B_1. At present it is still a matter of dispute whether this does or does not contain sulphur in the molecule. There seems little doubt that it is a nitrogenous base, of fairly simple molecular structure, and as such it will no doubt be shown to have specific colour and other reactions. Here, again, it would seem that the devising of tests for identification and estimation in mixed foodstuffs can only be a matter of time, though it may well be of some considerable time. About vitamins B_2, B_3, B_4, and *E*, and any others that may have been hypothecated to explain experimental results, it is at present not even possible to make reasonably cautious predictions.

It may then be said that a study of this Report might not seem very encouraging to the food analyst, but that a simultaneous consideration of the advances made since the Report was compiled definitely puts a different complexion on the matter. There is no more reason for him to take up a pessimistic attitude about the possibilities of chemical vitamin assay than about any other of the more difficult, and therefore more fascinating, analytical problems that have, it may be supposed, been sent to try him.

A. L. BACHARACH

DIZIONARIO PRATICO DEGLI ALIMENTI. By ETTORE SANTANGELO. Pp. 1+408. Milan: Ulrico Hoepli. 1932. Price 50 lire.

As is explained by a sub-title, not given above, this book is much more than a mere dictionary of foods, although this occupies the major part of the volume.

The author begins by discussing briefly the question of nutrition, including all metabolic processes occurring in the organism—feeding, digestion, absorption, cellular metabolism, and excretion. Next comes consideration of the various classes of food required, namely, proteins, carbohydrates, fats, inorganic materials, water, vitamins, and atmospheric oxygen. For the first four of these classes, the individual members are specified, and their sources, uses, and fate are described. The section on vitamins extends to only three pages, but forms a sufficient summary of present-day knowledge of these substances.

The dictionary of foodstuffs comprises nearly 300 pages and over 1000 items. Included here are not only all the foods, condiments and beverages in use in Italy, but also a great number of those employed in other parts of the world. The information given is comprehensive, and deals with the botany, zoology, chemistry, physiology, pathology, pharmacology, toxicology, and even gastronomy of the

different products. Not only is this part of the book of interest to the layman, but it would doubtless be found of use, for purposes of reference, by all concerned in the analysis of foods.

The final, and by no means least valuable, section consists of a number of diet charts, accompanied by a good deal of explanatory matter. The first division of these charts refers to diets for those in normal healthy condition, the cases of infants, adolescents, adults engaged in different occupations (sedentary or involving muscular fatigue in varying degree), players of games, old people, and women during the various stages of maternity, being considered separately. The second division is devoted to diets suitable for either children or adults suffering from various complaints, such as uricemia, gout, obesity, diabetes, tuberculosis, etc.

The matter is presented in an attractive manner, and any question on which divergent opinions are held, such as vegetarianism *versus* ordinary mixed diet, is discussed reasonably and without bias. Although, as stated above, the bulk of the book—the dictionary—is useful mainly for reference, the other sections will repay careful perusal. The print is excellent, the general appearance pleasing, and the price moderate; a good index is included.

T. H. POPE

GAS CALORIMETRY. By Major C. G. HYDE, M.C., A.R.C.S., F.I.C., and F. E. MILLS, B.Sc., A.M.I.Chem.E., with an Introduction by Professor C. V. BOYS, LL.D., F.R.S. Pp. xvi+376, 210 illustrations. London: Benn. Price 42s. net.

This excellent book is a timely reminder to the scientific public of the importance of the part played by gas calorimetry in the technical life of the country. Since 1920, all gas supplied in Great Britain has been sold by the therm, and its price per unit volume controlled by measurement of its calorific value by officially appointed examiners. A necessary corollary of this is that calorimetric measurements are an essential control test in every gas undertaking.

In spite of the importance of the subject, there had been no comprehensive book on the methods of gas calorimetry since the appearance in 1911 of *The Calorific Power of Gas*, by Coste. Various books, such as Levy's *Gasworks Recorders* (1922), have included valuable descriptions of some instruments, but detailed information as to modern methods has generally had to be sought in original papers or catalogues, or in the official publications of the Gas Referees. The present work thus supplies a need.

It is difficult, or impossible, to criticise an exhaustive treatise on a highly specialised subject, written with the authority of long and wide experience from both the production (Mr. Mills) and inspection (Major Hyde) sides of the gas industry. It is enough to say that the thoroughness with which every aspect of gas calorimetry is treated, and the wealth of detail given to the description of the structure and application of all the instruments in practical use, should make this, for many years, the standard work in this country, and probably throughout the world.

The number of pages given to various subjects may be cited:—Gas Measurement 28, Water Measurement 12, Thermometry 14. In the last, mention might have been made of the advantages, for calorimeter thermometers, of filling the space above the mercury with nitrogen at reduced pressure; in the reviewer's opinion,

solid stem thermometers are preferable to the enclosed-scale Beckmann thermometers recommended in the section on bomb-calorimetry. Forty-one pages are given to the different types of water-flow calorimeters, and one-hundred-and-forty to recording calorimeters. Some of these recording instruments are of extreme interest from the ingenuity of their design; the Boys Recorder, to which 34 pages are given, is explained fully for the first time.

In the section on the calculation of the calorific value of a gas from its composition, there is a remark on gas analysis which is slightly misleading:—". . . determining the hydrogen and methane by the method of explosion (now known to give somewhat unreliable results)." The facts are, that provided the proportions of the gases in the mixture exploded lie within certain rather narrow limits, admittedly difficult to ensure, accurate results are obtainable; but if, after the explosion, these proportions are shown to have been outside these limits, the result is then not to be relied upon.

From the point of view of craftsmanship it is a pity that no uniform system of references seems to have been followed, especially as this gives a quite false impression of hasty compilation, which the text of the book does not justify. For journals having volume numbers it does not seem necessary to give month and day references; it is also irritating to find volume numbers printed in two entirely different types on consecutive lines (p. 349). This, however, is a trivial blemish which can be corrected without difficulty in the next edition.

The numerous diagrams and photographs are clear and excellently produced; a number of useful graphs and nomograms are included, and the volume ends with 19 pages of tables.

The book would seem quite essential to all who have any practical concern with gas calorimetry; it also contains much information which makes it of value to workers in other fields.

H. R. Ambler

Chemical Arithmetic. By S. B. Arenson. Pp. v+108. London: Chapman & Hall. Price 7s. 6d.

This small volume is designed to familiarise elementary students with the usual chemical and related physical calculations, and, since the author possesses the gift of simple exposition and lucidity, the text will admirably serve its purpose. The instruction provided is expressed in an interesting manner, and is frequently enlivened and explained by unexpected, but apt, reference to some commonplace subject or calculation. In places, the mode of expression is decidedly transatlantic, but this is by no means so insistent as to be displeasing.

Several innovations are adopted relating to the solution of various problems, and these tend greatly to stimulate the deductive powers of the student. The problems, of which 308 are given, are well-selected, and the text, tables and index are accurate and reliable.

Much care has evidently been expended upon the production of this book, and it is well worth the attention of all engaged in the teaching of chemical arithmetic.

T. J. Ward

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