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The Freezing Point of Milk as a Means of Detecting Added Water.

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OSMOSIS so obviously occupies such an important rôle in the general metabolism of animals that it is not unreasonable to suppose that the osmotic pressures of various body fluids, particularly the blood, may be practically constant for different animals of the same species. The direct measurement of osmotic pressure with precision is difficult, and quite impossible under anything like routine conditions. It is well known, however, that the depression of the freezing point of a dilute solution is an indirect, though accurate, measure of the osmotic pressure, so that the idea underlying the application of the freezing-point method to milk analysis will be fairly obvious. If it be found, as a fact, that the osmotic pressure of the blood of all cows is practically identical, it will probably follow that the osmotic pressure of their milk will also be a constant quantity, and that, therefore, the freezing point of cows' milk, undiluted, will vary little from a mean value. If this be so, any addition of water to milk will produce an alteration in the freezing point, and will thus be detected.

Dreser (*Arch. exper. Pathol. Pharm.*, 1892, **29**, 303) found that the osmotic pressure of cows' blood was virtually constant, and his results were confirmed by Hamburger, Bugarszky and Tangl, von Korányi, Koeppe, Strauss, etc., whilst some of these investigators also reported the constancy of the freezing point of

milk. From this time, a large number of papers has been published, all testifying to the constancy of the freezing point of milk and its great value in the detection of added water. The only dissentient voice is that of Tocher (*Scottish J. of Agric.*, 1929, **12**, 405), who considers that the test is "scientifically unsound." Tocher's opinion, based upon his own results given in "Variations in the Composition of Milk," is founded on the examination of milks, some of which were admittedly sour when analysed. This fact, coupled with the further fact that his opinions are opposed to those of every other worker on this subject, rather discounts the value of his conclusions. From a consideration of the points discussed above, it would appear that this test is founded more specifically on a theoretical basis than those more usually applied.

The position of this subject up to the year 1914 has been ably summarised in *Food Report, No. 22, to the Local Government Board* (now the Ministry of Health) by G. W. Monier-Williams, which report also gives a full bibliography.

THE APPARATUS.—The determination of a freezing point to an accuracy approaching 0·001° C. is an operation in which certain special precautions must be taken. In the first place, a thermometer reading to this degree of accuracy is liable to various errors beyond the obvious one of inaccuracy of the calibration, which could, of course, be overcome by suitable control. Such errors are, variations in the volume of the bulb, the large size of the bulb requiring considerable time to become constant in temperature, the effect of the fine capillary (lag), and the temperature of the emergent column of mercury. Beyond possible inaccuracies introduced by the thermometer itself, other errors may be caused by radiation of heat during the experiment, production of heat by the stirring which is necessary, and the super-cooling of the freezing solution.

These errors may be overcome in two ways—either by making suitable corrections for each one of them, or else by carrying out the test under fixed empirical conditions and comparing unknown samples with those known to be genuine. The former of these two courses is certainly the more scientific, and was the one followed by Monier-Williams; the latter is, however, capable of giving very useful results in experienced hands, and, moreover, gives results not very far removed from the absolute, as some of the errors tend to neutralise one another.

The best-known method utilising this latter procedure is that of Hortvet (*J. Ind. Eng. Chem.*, 1921, **13**, 198; *J.A.O.A.C.*, 1922, **5**, 172, 470, 484; 1923, **6**, 424, 429), who designed an apparatus, based on that of Monier-Williams, which would give absolute, or nearly absolute, readings with a minimum of trouble. His apparatus, and the method of use, are described in the above-named papers, and also in the *A.O.A.C. Methods of Analysis*, 2nd edition, p. 265.

A more simple apparatus has recently been described by R. L. Andrew (ANALYST, 1929, **54**, 210), who uses the ordinary Beckmann cryoscope. This method, though possibly capable of giving useful results after considerable practice, has not been found, in our experience, to be very convenient.

Apart from the discomfort of working with mixtures of ice and salt, it is not easy to control the temperature of these with anything like exactitude, whilst the fact that it is necessary to make such mixtures from time to time also adds to the inconvenience of the method.

On realising the manipulative difficulties connected with all methods depending upon the use of ice and salt, which was the first method tried, we next turned our attention to the method of Hortvet which, it was thought, might offer considerable advantages, seeing that it depends on ether as a source of the necessary cooling. Up to the present, the advantages hoped for have been entirely realised, and we put forward our preliminary results in the hope that our experience will be of some interest to those who may be contemplating the use of a test which has become a standard method of examination in the Colonies, on the Continent of Europe, and in the United States of America. The apparatus was originally suggested by Hortvet in 1921.*

THE THERMOMETERS.—These are two in number, one for the cooling bath, graduated in degrees reading from +30° C. to −30° C.,† and another, the actual freezing-point thermometer, reading from +1·0° C. to −2·0° C. graduated in hundredths of a degree, the divisions being of sufficient size to allow of eye estimation to thousandths of a degree being carried out by means of a lens. The control thermometer can readily be standardised by comparison with a standard thermometer. The standardisation of the freezing-point thermometer is a more difficult matter. Before attempting this, the report of Monier-Williams and the papers of Hortvet should be read very carefully, so that the difficulties involved and the possibilities of error can be thoroughly realised.

(1) CALIBRATION.—When the thermometer is first cooled, it is not unlikely that it will be found that a portion of the mercury has been left behind in the safety bulb at the top. When the ordinary method of tapping and warming fails to connect the two portions of the thread, the following process may be tried with safety and with every likelihood of success:

The thermometer is clamped in a beaker of water (of not less than 500 c.c. capacity) and the water gradually heated by an ordinary Bunsen flame, the temperature of the water being controlled by another thermometer reading to 100° C. The temperature is allowed to rise slowly, the freezing-point thermometer being tapped from time to time until the rising thread and the detached globules of mercury in the upper safety bulb (or bulbs) have all joined together. The temperature of the water may be raised to 80° C., which should be as high as is necessary, without damage being done to the thermometer.

The preliminary standardisation may be carried out by placing the thermometer in melting ice and taking the reading when constant. It must be

* Until a short time ago, it was necessary to import this from America at a cost of something like £25, but it is now offered by Messrs. Gallenkamp in this country and sold by them at £14 14*s*. This price includes thermometers and all other necessary fittings complete.

† There would appear to be no reason why such a long range should be used. A thermometer having a shorter range, and divided into tenths of a degree, would appear to be more useful.

remembered, when taking readings with a thermometer of this type, that the thermometer must be tapped with some suitable light hammer—we use a large cork, cut square, fitted on to the end of an old cork borer, the metal stem being protected by means of a length of rubber tubing—until the reading remains constant.

In order to find the zero point of the thermometer it is necessary to determine the freezing point of recently boiled and cooled distilled water in the apparatus, under exactly the same conditions as those under which the freezing point of the milk is obtained. The details are given in full by Hortvet and the A.O.A.C. We have found their instructions to give excellent results. In order further to check the thermometer for any irregularities in the scale, it is necessary to take the freezing points of solutions, again under the same conditions as for milk, for which the figures are accurately known. Sucrose is a most suitable substance—it can readily be obtained in a high degree of purity (B.D.H., A.R.), and the freezing points of 7 w/v and 10 w/v solutions have been determined by the A.O.A.C., under the conditions of the Hortvet test, using Bureau of Standards tested thermometers. In Table I the A.O.A.C. figures are given, together with those obtained by us with two of our own thermometers.

TABLE I.

Sucrose in 100 c.c. Grms.	Freezing-point depression. A.O.A.C. Therm. 1. °C.	A.O.A.C. Therm. 2. °C.	E and S. Therm. 1. °C.	E and S. Therm. 2. °C.
7	0·422	0·422	0·426	0·423
10	0·622	0·621	0·625	0·621

It should be emphasised that the figures obtained by the A.O.A.C. were with a standardised thermometer, whilst those obtained by us were with unstandardised thermometers, although, of course, allowance was made in each case for the variation of the freezing point of water from 0° on the scale.

The freezing point depressions of these cane sugar solutions thus obtained are about 0·02° C. greater* than those calculated from Raoult's formula and those actually determined by Monier-Williams. The average freezing-point depression for milk obtained in the Hortvet apparatus, 0·555° C., is also about 0·02° C. greater than that obtained by Monier-Williams, 0·5375° C. It may be that Monier-Williams' figures are nearer the absolute freezing point (this seems to be doubted by Hortvet), but most observers agree with the greater figure. In any case, however, workers should always calibrate their own apparatus with milks of known purity, so that no difficulty or inaccuracy can arise from this source. It is quite likely that these differences are due largely to the fact that Monier-Williams applies corrections for super-cooling, etc., whilst Hortvet† and most other workers do not.

* The "depressions" are greater, the freezing points are lower. This should be made clear. *Cf.* footnote on p. 2 of the L.G.B. Report.

† In the Hortvet process, super-cooling is always carried out to the same extent.

(2) THE CHANGE OF THE ZERO.—It is well known, of course, that the zero point of a thermometer may continue to rise for months, and even years, after the thermometer has been made, owing to the slow rate at which glass recovers its original volume after being heated. The same phenomenon, although to a less marked extent, is noticed after a thermometer has been heated to a moderate temperature; and further than this, very slight changes, of the order of a few thousandths of a degree, may be noticed from day to day, or even from hour to hour. Any thermometer, therefore, which is used for freezing-point determinations should have its zero checked repeatedly, at least once each day, and a record should be kept of the readings which are observed. Up to the present, the authors have used two thermometers,* which may be distinguished as No. 8 and No. 12. They have been examined on many occasions, both in melting ice and in the Hortvet apparatus. A few of these results, showing the changes likely to be encountered, are set out in Table II. Both thermometers had to be heated to 70°–75° C., in order to join up the threads; the number of days given in the table refers to the period which elapsed after this heating was carried out.

TABLE II.

ZERO POINT OF THERMOMETERS.

No. 8.			No. 12.		
	Zero in Hortvet apparatus.			Zero in Hortvet apparatus.	
No. of days after heating.	Beg. of day.	End of day.	No. of days after heating.	Beg. of day.	End of day.
7	+0·025	—	55	−0·028	—
9	+0·016	—	56	−0·020	—
10	+0·021	—	57	−0·020	−0·020
13	+0·027	+0·024	58	−0·020	−0·020
14	+0·027	+0·028	60	−0·020	—
43	+0·035	+0·031	62	−0·020	—
44	+0·031	+0·026	65	−0·020	—
45	+0·030	+0·027	67	−0·025	—
69	+0·017	+0·017	69	−0·022	−0·022
70	+0·019	+0·010	70	−0·022	−0·021

There is some evidence that changes in barometric pressure affect the zero point, but this factor is apparently complicated by the existence of other factors, and sufficient readings have not yet been taken to decide finally on this point.

The zero is sometimes lower at the end of the day than at the beginning, but the change is apparently influenced by the temperature at which the thermometer is kept between the readings: whether at laboratory temperature or at

* A few experiments have been carried out with a Beckmann thermometer, but this type is not so convenient as that described above.

about the freezing point. The following readings given in Table III illustrate this point:

TABLE III.

CHANGE IN ZERO FROM MORNING UNTIL EVENING.

Time.	Thermometer 8.		Thermometer 12.	
	Kept cold during day.	Kept at lab. temp. during day.	Kept cold during day.	Lab. temp. during day.
Beginning of day	+0·017	+0·019	−0·022	−0·022
End of day	+0·018	+0·010	−0·021	−0·022

In order to obtain further information concerning these changes, readings of thermometer 8, the one showing variations, were taken every hour under each of these conditions. In one case the thermometer was allowed to rise to the laboratory temperature, and in the other the thermometer was only allowed to rise sufficiently above the freezing point (say 1–2 degrees) to ensure the melting of the ice, and this only for a few moments before each determination. The results obtained are given in Table IV.

TABLE IV.

DETERMINATION OF ZERO EVERY HOUR.

Time a.m.	Thermometer 8.	
	Kept at lab. temperature between readings.	Kept cold between readings.
10·0	+0·030	+0·025
11·0	+0·029	+0·025
12·0	+0·022	+0·025
1·0	+0·021	+0·024
2·0	+0·018	+0·022
3·0	+0·019	+0·022
4·0	+0·018	+0·022
5·0	+0·020	+0·022

From these results it would appear that it is essential to take repeated readings of the zero of all thermometers until the behaviour of each one has been thoroughly investigated. After this, the zero should be observed as often as the previous results obtained appear to demand.

THE METHOD.—With water and cane sugar solutions, the freezing takes place spontaneously without the addition of ice as a starter, but in the case of milk such a starter is usually necessary. We have followed the technique of Hortvet*

* Careful experiment has shown that considerable variations in the temperature of the control thermometer, the volume of ether, and the amount of stirring exercise very little, if any, effect on the results obtained.

with excellent results. The addition of a small piece of ice, in the case of milk, is a little difficult at first, but becomes quite easy with practice. We have evolved the following details:

The metal rod to hold the fragment of ice and an opened pen-knife are placed in crushed ice close to the right hand of the operator. A small piece of ice is placed on a clean folded towel on the bench between the operator and the apparatus, and covered with another portion of the towel. When the milk has been cooled to within 0·2° of the required temperature, the ice is wiped dry with the towel, and a few small fragments of ice are scratched from the piece with the knife. When the temperature is within about 0·05° C. of that required, the starting rod is removed from the crushed ice, wiped quickly with the towel, and one of the fragments of ice taken up and transferred to the freezing-point tube. By this method one worker can carry out the whole of the manipulations necessary without any difficulty.

THE ACCURACY OF THE READINGS.—The thermometers supplied with the ordinary form of the Hortvet apparatus are, as stated above, graduated in hundredths of a degree* so that it is possible to estimate to thousandths of a degree. It is, however, somewhat difficult to overcome parallax, particularly when the mercury is about midway between two divisions, and at these points there is a possibility of an uncertainty of the order of a thousandth of a degree in the actual reading of the thermometer. Apart from this, we have found no difficulty in agreeing with each other in duplicate experiments on the same sample. There is not the slightest difficulty in obtaining duplicate readings which do not differ by more than two-thousandths of a degree. The usual error is less than this, and is almost entirely due to the difficulty of parallax already mentioned (Table V).

When the freezing point is determined it occasionally happens that the mercury only remains at the highest point sufficiently long to take a rough reading. Such experiments should be discarded, as we have found that these, even when the reading can be taken, frequently give too low a freezing point.

TABLE V.

No. of sample.	Freezing-point depression.	
	J.R.S.	G.D.E.
2074 W.D.	0·478	0·477
2087 W.D.	0·498	0·498
2088 W.D.	0·518	0·518
1062 O.D.	0·534	0·534
1550 By.D.	0·545	0·545
1088 Rs.D.	0·551	0·553
Sugar solution ..	0·428	0·428
Do.	0·488	0·489
Do.	0·525	0·525

* Each degree occupies 9–10 cm. on the scale.

THE RESULTS OBTAINED.—Under this heading the results obtained for known genuine milks are collected. Firstly, those published by other workers, both in the Hortvet apparatus and also by other means; secondly, those which have been obtained in the Hortvet apparatus by ourselves.

(1) *By previous Workers.*—Many results by previous workers are given in the report of Monier-Williams and in the paper by Hortvet in the *Journal of Industrial and Engineering Chemistry*. These results, together with others obtained since the above papers were published, are collected in tabular form below:

TABLE VI.

FREEZING POINT DEPRESSION. (VARIOUS OBSERVERS.)

Observer.	Average.	Ordinary range.	Extreme range.
Dreser	—	0·55 –0·57	—
Winter	0·555	0·55 –0·56	0·54 –0·57
Bordas and Génin	—	0·512–0·529	—
Henderson and Meston (1913)	0·550	0·54 –0·56	—
Henderson (1929)	—	0·545–0·55	0·545–0·565
Monier-Williams*	0·537	0·53 –0·55	0·519–0·558
MacLaurin	0·550	—	0·545–0·565
Ducros and Imbert	—	—	0·533–0·575
Hummelinck	—	—	0·542–0·570
van Raalte	—	—	0·540–0·570
Keister	—	—	0·541–0·574
Gooren	—	—	0·530–0·570
Hortvet	0·548	0·545–0·562	0·534–0·562
Atkins	0·550	0·52 –0·56	0·544–0·556
Stoecklin	—	0·53	—
Leather	—	—	0·529–0·57'
Reicher	—	0·550–0·580	0·541
Bailey	—	0·530–0·562	0·530–0·56·
Joseph	—	—	0·538–0·57·
Bolm	0·550	—	0·530
Gronover and Türk	—	0·540	—
Koenig and Kluge	—	0·540	—
Klamer	—	0·53 –0·55	0·52 –0·56
Ficke and Kordatyki	0·552	0·537–0·576	—
Andrew	0·555	0·550–0·560	0·545–0·565
Tocher*	0·548	0·525–0·620	0·505–0·784
Buchanan & Lowman	—	—	0·537–0·582
Filippo	—	0·53 –0·54	—

* In these cases the Raoult correction has been applied. This will reduce the figure obtained by about 0·010. Without this correction Tocher's average becomes somewhat greater than that of other observers. This may be due to some of his samples being sour.

With the exception of those of Tocher, the above results show an extreme variation of 0·070, *i.e.* from —0·512 to —0·582. It is, however, unsatisfactory to take the extremes obtained by various observers, as they include results by different methods and the corrections which have been applied are not uniform. The highest variation found by any one other observer is 0·048 and, in general, this figure is not more than 0·03. Whatever may be finally decided as to the specific utility of the test, the variations in the results obtained under properly controlled conditions are certainly very much less than those given by any other method.

(2) *By the present Authors.*—For some time now, many of those samples of milk examined by us which have shown any point of interest have had their freezing points determined. In all cases where this determination gave a low result, or where, for any reason, the sample appeared to be suspicious, a comparison sample was taken, usually from the cows, but sometimes on delivery. The results so far obtained are given below:

TABLE VII.

Number.	Original Sample.			Comparison Sample.			Remarks.
	Solids-not-fat.	Acidity.	Freezing point.	Solids-not-fat.	Acidity.	Freezing point.	
1075 Rs.D.	7·6	2·3	−0·464	9·1	2·4	−0·553	5 cows
1504 L.D.	6·8	1·4	−0·398	9·1	1·9	−0·547	3 cows
1505 L.D.	8·6	1·9	−0·524	8·6	2·2	−0·540	? cows
2074 W.D.	8·1	1·7	−0·477	9·1	2·2	−0·538	On delivery
2103 W.D.	8·8	2·0	−0·521	9·1	2·0	−0·542	16 cows
2087 W.D.	8·4	1·9	−0·498	8·7	1·9	−0·542	? cows
2088 W.D.	8·5	1·7	−0·518	8·9	2·1	−0·543	? cows
1346 S.D.	7·5	1·7	−0·452	9·5	1·8	−0·548	7 cows
74 Lytham St. Annes	7·1	1·6	−0·447	9·1	2·3	−0·553	? cows
713 C.D.	7·4	1·8	−0·453	8·7	2·2	−0·559	12 cows
1353 S.D.	8·1	1·8	−0·509	8·6	2·1	−0·542	9 cows
1313 Km.D.	7·8	2·1	−0·475	8·6	2·3	−0·540	? cows
1321 Km.D.	8·2	1·9	−0·499	9·0	2·4	−0·540	On delivery
1045 O.D.	9·0	2·2	−0·530	9·1	2·5	−0·540	24 cows
1046 O.D.	8·8	2·2	−0·531	8·9	2·2	−0·534	
721 N.L.D.	8·1	3·6	−0·519	9·2	2·7	−0·540	2 cows
1542 By.D.	8·4	2·2	−0·510	8·7	2·1	−0·543	4 cows
1543 By.D.	8·7	1·9	−0·526	8·6	2·2	−0·543	
1801 R.D.	8·2	1·8	−0·497	9·1	2·2	−0·544	? cows
1822 R.D.	9·1	2·6	−0·533	9·0	2·5	−0·533	? cows
725 C.D.	9·0	2·3	−0·533	9·1	2·3	−0·538	43 cows
726 C.D.	8·7	1·9	−0·541	8·3	1·9	−0·544	? cows
727 C.D.	8·7	2·1	−0·533	8·2	1·7	−0·543	2 cows
729 C.D.	9·3	2·2	−0·533	9·2	2·1	−0·531	? cows
731 C.D.	8·1	2·2	−0·498	8·8	1·9	−0·552	21 cows
1431 Bn.D.	8·1	2·2	−0·503	9·0	2·4	−0·541	26 cows
1432 Bn.D.	8·7	1·9	−0·524	8·5	4·4	−0·553	8 cows
1751 A.D.	8·9	2·2	−0·523	9·1	2·2	−0·541	? cows
1509 Wgn.D.	8·8	2·1	−0·524	9·01	1·9	−0·542	? cows

In nearly every case the depression obtained from the comparison sample has been higher than that from the original sample. From the ordinary determination of the solids-not-fat, samples 1505 L.D., 2103 W.D., 2088 W.D., and 1543 By.D., would have been passed as genuine, whilst 2087 W.D. and 1542 By.D. are only slightly below the minimum limit. The freezing point, however, suggested the addition of appreciable quantities of water in each case, additions which were confirmed in each case by the comparison sample.

In addition to the figures given in Table VII, we have determined the freezing point of some 50 other milks of which the history was not known, but which were apparently genuine. The figures obtained have varied from −0·533 to −0·555, with an average of −0·543. These figures agree fairly well with, but are apparently a little lower than, those of Hortvet, whose range was 0·534 to 0·562, with

an average of 0·548. Such difference as there is, however, is of little, if any, significance. For the present it may be assumed that an average of 0·54 may be taken for the purpose of calculating added water, but that no milk should be considered as watered on the evidence of the freezing point of a single sample alone, unless the depression falls below 0·53.

It seems to be fairly well established that as a milk becomes sour the depression of the point increases, so that the method is only applicable to fresh milks or slightly sour milks after suitable correction. All the freezing points determined by us have been obtained on fresh milks. The acidities given are in ml. of *N*/10 sodium hydroxide for 10 c.c. of milk.

As far as our results have gone at the moment, we can confidently recommend the use of Hortvet apparatus as a convenient and rapid process for the determination of the freezing point of milk. We believe that the results obtained will be of considerable value in the detection of added water.

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The Routine Detection of Nitrates in Milk.

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(*Read at the Meeting, April* 2, 1930.)

The reasons why the test for nitrates in milk, as an aid to the detection of added water, has been neglected, are probably as follows:—(i) Statements have been made that cows drinking water containing nitrates in amounts which are frequently met with, will yield milk giving a reaction for nitrates (Analyst, 1894, **19**, 83). This erroneous impression was doubtless due to faulty manipulation of the particular test employed. H. Kranze (*Arch. Hyg.*, 1925, **85**, 271; Analyst, 1926, **51**, 255) states that the milk of cows which for 30 days had been drinking water containing 13 parts of nitric nitrogen per 100,000 was free from nitrate. His results are in agreement with my practical experience, namely, that genuine cows' milk, from whatever source, will not normally give a nitrate reaction.

Attention is called here to a remarkable statement by E. Kohn-Abrest and S. Kawa-kibi (*Compt. rend.*, 1926, **183**, 522; Analyst, 1926, **51**, 585) that, using a nitrometer method, they found in six determinations 80, 80, 69, 80, 0, 0 mgrms. of nitric nitrogen (as N_2O_5) per litre of cows' milk, and 193 and 145 mgrms. in human milk.

They say, with reference to the former:—"It would be interesting to determine the origin of the nitrates in milk, but, from now on, their presence can by no means be regarded as an indication of watering; the nitrate content of milk is decidedly higher than that of potable waters, and higher even than many highly polluted ones."

While this statement is quite incorrect, I am not at the moment prepared to state the source of the error; it is, however, of interest to note that they found much larger quantities of nitrate in human than in cows' milk. The presence of nitrates in human milk is in agreement with my experience, although the quantities given above are undoubtedly too high. All the samples of human milk (five) tested in this laboratory gave a positive reaction for nitrate by the diphenylamine test.

Kohn-Abrest and Kawa-kibi observe (rather strangely) that the ordinary foods are fairly free from nitrates, and conclude, therefore, that the human organism normally elaborates notable quantities of nitrates which are eliminated by the kidneys and, in the case of nursing mothers, by the mammary glands.

Incidentally, human urine responds to the diphenylamine test much more strongly than the specimens of human milk which I have examined.

(ii) Nitrates may be given to cows medicinally, and thus be secreted in their milk.

I consulted a veterinary authority who is an Inspector under the Diseases of Animals Acts, and he stated that he was not aware of nitrate in any form being at all commonly given to cows, though it might be given to cows affected with cough or fever.

(iii) A third reason for the lack of popularity of the test for nitrates in milk is its apparent unsuitability, when viewed as, say, a semi-routine method. With the procedure which I have adopted, one or more milks may be tested, together with a control, in three or four minutes, with little trouble.

THE DIPHENYLAMINE TEST FOR NITRATES.—According to Thorpe's Dictionary, this test was first applied to milk serum by Soxhlet, and the humorous observation follows that, "The test has been frequently re-discovered." Briefly, the test consists in adding a solution of diphenylamine in sulphuric acid to milk serum, a blue colour indicating the presence of nitrate or nitrite. J. Tillmans (*Z. Untersuch. Nahr. Genussm.*, 1910, **20**, 676; ANALYST, 1911, **36**, 67) has examined the method and recommended various modifications, as also have Elsdon and Sutcliffe (ANALYST, 1913, **38**, 450). The latter workers were chiefly concerned with nitrate added to milk as a preservative, and not due to added water. I have modified the methods of these workers to produce a rapid and reliable method for routine purposes.

ROUTINE METHOD FOR DETECTION OF NITRATES IN MILK.—The reagents required are as follows:

(1) *Mercury Reagent.*—This consists of an aqueous solution containing 20 per cent. of mercuric chloride, 5 per cent. of ammonium chloride, and 20 per cent. (by volume) of concentrated hydrochloric acid. (The presence of ammonium chloride is necessary to keep the mercuric chloride in solution.)

(2) *Diphenylamine Reagent.*—(Elsdon and Sutcliffe.)—Diphenylamine (0·085 grm.) is mixed with 50 c.c. of water, and 450 c.c. of concentrated sulphuric acid are gradually added.

Six or seven drops of mercury reagent are added to 4 or 5 c.c. of milk in a test tube (previously washed with some of the milk), the tube shaken occasionally during 2 minutes, and the mixture filtered through a 9 cm. paper (previously washed with distilled water) into a test tube (6 inches by $\frac{1}{2}$ inch) containing about 2 c.c. of diphenylamine reagent. (This should be introduced into the test tube by means of a pipette, *i.e.* without unduly wetting the sides with the reagent.)

The filtration should be conducted with the test tube containing the diphenylamine in an oblique position, so that the filtered milk serum which is usually quite clear, falls on to the side of the tube and flows on to the surface of the reagent fairly gently, so as not to mix with it to any great extent. When about 1 c.c. of serum has collected, the funnel is removed and the test tube is held vertically and examined against a white glazed surface.

With normal milk the line of demarcation between serum and reagent is without colour, and, upon very gently mixing at the point of contact, a faint yellow colour appears, changing to dark brown as charring increases.

With a milk containing fairly large amounts of nitrate, the surface of contact between serum and reagent forms a dark blue layer, which colour spreads upwards on gentle agitation.

When smaller quantities are present (*i.e.* of the order of 0·1 part of nitric nitrogen per 100,000 or less) the appearance is at first similar to that of normal milk, but, on gently agitating, the blue colour appears at the bottom of the serum, while immediately underneath, and slightly later, appears the yellow ring as with normal milk.

PRECAUTIONS TO BE OBSERVED.—Practically all laboratory reagents which are kept in a room where strong nitric acid is kept and used will give a positive test for nitrates. The reagents intended for this purpose, therefore, should not be kept in such a place, otherwise in a week or two it will be necessary to prepare fresh ones.

Test tubes should be washed with distilled water and kept out of the main laboratory.

One or two tests with genuine milk should always be made alongside the sample to be tested, and weak positive reactions should always be repeated. Incidentally, it must be remembered that the diphenylamine test is not specific for nitrates, but is common to most oxidising agents (including peroxides), and is also given by formaldehyde.

RESULTS OBTAINED IN PRACTICE.—The method described will detect the addition of 5 per cent. of a water containing about 0·5 part of nitric nitrogen per 100,000, but the delicacy can be increased, if required, by working on a larger quantity of milk and concentrating the serum. The test is applied in this laboratory to all samples of milk containing less than 8·5 per cent. of solids-not-fat; out of 1172 samples taken from June to November of last year, 102 were below 8·5 per cent., and 50 of these gave a positive reaction for nitrate.

Seventy-seven samples were below 8·4 per cent., and of these, 46 showed nitrates present. Sixteen samples, containing more than 8·0 per cent. of solids-not-fat, contained nitrates.

It seems extremely likely that, when the difference in solids-not-fat between a prosecution sample and the "appeal-to-the-cow" sample is not very great, the nitrate test may frequently provide a very adequate reply to the "natural variation" defence.

Nitrates have also been detected in cream by this method; the sample in question was sterilised cream, but was only slightly deficient in solids-not-fat. In this connection it may be noted that artificial cream may quite possibly contain nitrates; their presence would, at any rate, afford some additional evidence as to the artificial nature of the cream.

I am indebted to the Birmingham City Analyst for permission to publish this paper.

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Sources of Error in the Determination of Hydrogen in Gases.

By H. R. AMBLER, B.Sc., F.I.C.

THE usual and the most convenient method of determining hydrogen in gases is to add excess of air or oxygen and explode. Within certain limits this procedure gives good results, but outside these limits it is liable to important sources of error. Numerous data have been obtained, as detailed below, to determine the magnitude of such errors and the conditions under which they are appreciable, and also to check the degree of possible error in the alternative slow-combustion methods. The points investigated are:—(1) Oxidation of nitrogen in the explosion method; (2) Oxidation of nitrogen by sparks; (3) Oxidation of nitrogen in the slow combustion method; (4) Completeness of combustion in the explosion method; (5) Completeness of combustion in the explosion method in the presence of methane.

INTRODUCTION.—In the determination of hydrogen by explosion with air or oxygen, errors may be introduced from two sources:

(1) By the oxidation of nitrogen that is usually present. This causes an additional contraction, making the figure for hydrogen too high. Varying quantities of nitrogen peroxide thus produced dissolve in the moisture in the explosion bulb, or react with the mercury. The remainder will subsequently be absorbed in alkali and will be recorded as methane.

(2) By incomplete combustion, hydrogen being in such cases left, even when excess of oxygen has been added (Hempel, *Methods of Gas Analysis*, 1892, p. 101).

Bunsen, using a eudiometer tube as explosion vessel, exploded various mixtures of electrolytic gas and air; he found that unless the proportion of electrolytic gas to air was more than 64 to 100 (*i.e.* 26 per cent. of hydrogen in the total gas) the error due to oxidation of nitrogen was negligible. If the proportion was less than 26 to 100 (*i.e.* 14 per cent. of hydrogen), combustion of the hydrogen was not complete. Hempel (*loc. cit.*, p. 101) states that these limiting proportions depend considerably on the conditions of explosion.

OXIDATION OF NITROGEN IN THE EXPLOSION METHOD.—White (*J. Amer. Chem. Soc.*, 1901, **23**, 476), using a modified Hempel explosion pipette, found that within Bunsen's limits the formation of oxides of nitrogen might still be large enough to introduce appreciable error into the hydrogen and methane figures. Error could be neglected only when the percentage of hydrogen was below 16·5. Even with the slow combustion method described by Dennis and Hopkins (*J. Amer. Chem. Soc.*, 1898, **21**, 398), oxidation of nitrogen was considerable. Jones

and Parker (*J. Ind. Eng. Chem.*, 1921, **13**, 1154), on the other hand, found that with the latter method this error was negligible, while by the explosion method (in a Morehead burette) the amount of nitrogen peroxide produced, even from a mixture containing 50 per cent. of hydrogen, was only 0·16 per cent. of the explosive mixture. With 30 per cent. of hydrogen, the NO_2 was entirely negligible (less than 0·001 per cent.).

I have found up to 1 per cent. of fictitious methane after exploding mixtures containing 30 per cent. of hydrogen, and appreciable quantities in weaker mixtures. In view of these disagreements, the following experiments were carried out to ascertain the conditions under which satisfactory determinations of hydrogen and small quantities of methane could be made with the apparatus in question.

Experimental.

Mixtures of hydrogen, oxygen and nitrogen were fired as follows:—(*a*) Mixtures with a total volume 10 c.c. in an approximately spherical bulb of 30 c.c. capacity at atmospheric pressure over mercury.

(*b*) Mixtures with a total volume 40 c.c. in a spherical bulb of 150 c.c. capacity at atmospheric pressure over mercury.

After explosion (initiated by a spark) the bulbs were washed out with water, the water run out into a small beaker, diluted if necessary, and treated with Griess reagent. The colour was matched by running into a similar vessel containing the same amount of water and Griess reagent, sodium nitrite solution (0·002 *N*) from a burette. Two molecules of NO_2 produce one of nitrous acid, and hence the amount of nitrogen peroxide formed in the explosion was estimated. It is to be borne in mind that this gives no indication of any nitric acid that might be formed directly in the explosion, and hence gives only lower limits of the extent of oxidation of nitrogen. It is considered, however, that at atmospheric pressure the amount of nitric acid so formed would be negligible. Results, which are given in Table I, show:—

(1) In both bulbs the amounts of nitrogen peroxide are considerably greater (for mixtures containing more than 20 per cent. of hydrogen) than those found by Jones and Parker.

(2) For mixtures containing less than 20 per cent. of hydrogen the error so caused in gas analysis will be negligible. Above this, the amount of nitrogen peroxide increases rapidly with increase of hydrogen content.

(3) The relative amount of nitrogen peroxide formed is greater in the smaller bulb. This is in agreement with the theoretical consideration that this (endothermic) reaction is favoured by rapid cooling, this being more rapid in the smaller bulb in which the ratio of surface of bulb to mass of gas is greater.

(4) The production of an appreciable amount of nitrogen peroxide coincides roughly with a flash in the explosion visible in daylight. In the cases

under discussion, where there was no visible flash, there was no appreciable NO_2.

(5) If there is an excess of hydrogen instead of excess of oxygen, the amount of nitrogen peroxide is inappreciable, even if the total proportion of $(2H_2+O_2)$ is very high.

(6) Provided there is excess of oxygen, the O_2/N_2 ratio is not important from the point of view of analysis.*

TABLE I.

FORMATION OF NO_2 IN THE EXPLOSION OF HYDROGEN-OXYGEN-NITROGEN MIXTURES.

Percentage composition of explosive mixture.			NO_2 produced expressed as percentage on explosive mixture.		
Hydrogen.	Oxygen.	Nitrogen.	Total volume 10 c.c. Per Cent.	Total volume 40 c.c. Per Cent.	Remarks.
17	34	49	—	0·002	No visible flash.
17·5	14	68·5	—	0·012	
18	14	68	—	0·008	
18·5	79	2·5	—	0·004	
20	14	66	0·03	0·02	
20	29	51	—	0·02	
20	40	40	0·01	0·007	
20	70	10	0·01	0·007	
22	16	62	0·2	—	
25	15	60	0·45	0·35	Slight flash.
25	15	60	0·06	0·007	No visible flash.
25	15	60	—	0·05	Slight flash.
25	55	20	0·36	0·13	
25	55	20	0·30	0·25	
25	70	5	0·45	0·11	
25	73	2	0·30	—	
30	20	50	1·8	1·8	Bright flash.
30	35	35	1·3	0·9	
30	60	10	0·4	0·3	
40	35	25	1·8	1·1	Very bright flash.
40	54	6	1·8	1·6	
45	25	30	2·0	—	
49	28	24	3·0	—	
52	47	1	5·0	—	
59	39	2	—	1·6	
62	20	18	—	0·01	Insufficient oxygen.

CONDITIONS GOVERNING FORMATION OF OXIDES OF NITROGEN.—In order for appreciable quantities of nitrogen peroxide to be produced it is necessary for

* It is seen, however, that there is slightly more nitrogen peroxide formed where there is a large proportion of nitrogen than where there is a large proportion of oxygen.

temperatures to be attained at which the velocity of the action $N_2+O_2=2NO$ is sufficiently rapid for appreciable action to occur during the explosion. Data of Jellinek (*Z. anorg. Chem.*, 1906, **49**, 229),* show that the time taken for half equilibrium quantities of NO to form is as follows:—1627° C., 2·08 minutes; 1827° C., 5·06 seconds; 2227° C., 0·01 seconds.

The temperatures of explosion can be calculated from a knowledge of the heat evolved and of the specific heats of the reacting gases. For a mixture containing 20 per cent. of hydrogen this calculation gives 2020° C. This is assuming, as is approximately the case with spherical bulbs connected with relatively constricted tubing, that the explosion takes place at constant volume. This, however, is not strictly the case, and hence the calculated figures should be slightly lower. It is clear that for mixtures richer than 20 per cent. oxidation of nitrogen will be appreciable. In the eudiometer tubes used by Bunsen, the conditions approximated to those of constant pressure, and the explosion temperatures of similar mixtures would be lower; thus he exploded mixtures containing 26 per cent. of hydrogen without oxidation of nitrogen. At strictly constant pressure the temperature attained with this mixture (26 per cent. of hydrogen) would be 1920° C.

Oxidation of Nitrogen by Sparks.—To test how much nitrogen peroxide may be produced by the initiating spark, the following experiment was carried out: Ten c.c. of air were admitted to the smaller bulb (10 c.c.), and sparks passed for 30 minutes. The spark gap (platinum electrodes) was about $\frac{1}{8}$ inch and the wattage about 5. The amount of nitrogen peroxide produced was about 1 c.c., that is, 10 per cent. of the original volume of the gas. This is equivalent to about 0·001 c.c. per second. It follows that:—(1) The oxidation of nitrogen produced by the momentary spark (about $\frac{1}{2}$ second) may be neglected as a source of error in analysis. (2) On the other hand, the method of prolonged sparking, which has sometimes been recommended for non-explosive mixtures, is always liable to large errors.

Oxidation of Nitrogen in the Slow Combustion Method.—White (*loc. cit.*) found appreciable quantities of nitrogen peroxide to be produced in the slow combustion of hydrogen. Positive results were obtained by the Griess test when the platinum wire was heated in air for 2 minutes. Contractions of up to 0·12 c.c. were obtained, and up to 0·3 c.c. produced of a gas soluble in alkali (total volume of air, 80 c.c.).

Rhodes (Dennis, *Gas Analysis*, 1913, p. 153), on the other hand, finds that this source of error is negligible. Jones and Parker (*loc. cit.*) come to a similar conclusion. This was confirmed again by the following experiments:—

Formation of Nitrogen Peroxide by Heating Spiral in Air.—The combustion pipette was of 30 c.c. capacity and carried a coil of 4 inches of platinum-iridium wire of diameter 0·1 mm. This was heated, the pipette containing air at atmospheric pressure. The pipette was subsequently washed out with water, and this tested with Griess reagent, and a blank titrated with 0·002 *N* sodium

* See also Jones and Parker, *loc. cit.*, and Hauser, *Bull. Soc. Chim.*, 1923, **33**, 1205.

nitrite solution as before. Positive, but very small, results were obtained as follows:—

TABLE II.

HEATING OF WIRE IN AIR. RESULTS OF GRIESS TESTS.

	NO_2 produced. c.c.
Wire heated at dull redness for 5 minutes	0·00005
,, ,, at bright ,, ,, 5 ,,	0·0001
,, ,, at bright orange colour 5 ,,	0·0001
,, ,, at bright yellow colour 5 ,,	0·0001

The same results were obtained when water containing Griess reagent was present in the combustion pipette during the heating.

As a further test, measured volumes of air were introduced into the pipette and measured again after the wire had been heated. The volume measurement was sensitive to about 0·003 c.c.

TABLE III.

HEATING OF WIRE IN AIR. CONTRACTION.

	Contraction observed. c.c.
Wire heated for 5 minutes at orange colour ..	0·003
,, ,, ,, 5 ,, ,, ,, ,, ..	(0·006)
,, ,, ,, 10 ,, ,, ,, ,, ..	0·003
,, ,, ,, 10 ,, ,, ,, ,, ..	0·003
,, ,, ,, 15 ,, ,, ,, ,, ..	0·000

COMPLETENESS OF COMBUSTION IN THE EXPLOSION METHOD.—As stated previously, Bunsen found that if mixtures contained less than 14 per cent. of hydrogen the combustion was not complete. Hempel (*Methods of Gas Analysis*, p. 101) states that an incomplete explosion can be recognised by sight, the flame visibly moving; he also states that the worst that can happen as a result of the hydrogen content being too low, is a non-explosive mixture. White (*loc. cit.*) finds that the slow combustion method gives slightly higher figures than the explosion method, and also that with the latter, slightly higher figures are obtained when hydrogen is exploded with oxygen than when air is used. To examine the magnitude of any possible errors due to this, various mixtures containing precisely measured quantities of hydrogen were exploded, and the contraction measured.

Experiments were made with total volumes of (1) *circa* 13 c.c., (2) *circa* 65 c.c. The apparatus was of the all-glass type; for the smaller quantities the apparatus used was that which I have described elsewhere (ANALYST, 1929, **54**, 517), and for the larger quantities a larger apparatus of the same general type. The hydrogen was prepared electrolytically and had been freed from oxygen either with alkaline pyrogallol or by treatment with the hot wire.* Results are given in Table IV.

* There was no noticeable difference in the results with hydrogen purified with pyrogallol and with the hot wire. (Expts. 9, 10, 11, 15, and 16, Table IV.) Hence it appears that the formation of carbon monoxide from the pyrogallol was in these cases negligible. Separate experiments showed that the amount of carbon monoxide so liberated was about 0·05 per cent., a proportion too small to show in this case.

TABLE IV.

COMPLETENESS OF EXPLOSION OF HYDROGEN.

Percentage composition of explosive mixture.			$\frac{\text{Hydrogen found}}{\text{Hydrogen added}} \times 100$.		
Hydrogen.	Oxygen.	Nitrogen.	Total vol. 10 c.c.	Total vol. 50 c.c.	
5·7	19·2	75·1	25		Definite explosion.
8·4	18·7	72·9	56		,, ,,
8·7	18·6	72·7	93		,, ,,
9·0	18·6	72·4	99·7		,, ,,
9·3	18·4	72·3	94		,, ,,
9·9	18·4	70·7	99·7		,, ,,
10·0	18·4	70·6	—	95·2	,, ,,
11·0	68·0	21·0	—	99·1	,, ,,
13·5	18·2	68·3		99·6	,, ,,
13·9	18·1	68·0		99·2	,, ,,
14·0	18·1	67·9		99·2	,, ,,
15·0	11·0	74·0	99·7	99·4	,, ,,
16·0	82·0	2·0		99·7	,, ,,
16·7	23·0	60·3		99·3	,, ,,
16·8	15·0	68·2		99·7	,, ,,
17·0	15·0	68·0		99·7	,, ,,
17·0	81·0	2·0		99·3	,, ,,
17·5	32·5	50·0		99·4	,, ,,
17·7	16·8	65·5		99·1	,, ,,
18·0	16·7	65·3		99·6	,, ,,
18·4	79·6	2·0		99·1	,, ,,
20·0	12·0	68·0		99·5	,, ,,
20·0	16·4	63·6		99·4	,, ,,
20·5	16·3	63·2		99·4	,, ,,

These results show:—(1) For mixtures containing from 10 per cent. to 20 per cent. of hydrogen, at least 99 per cent. of this hydrogen is oxidised.

(2) For poorer mixtures, combustion may be by no means complete, even when there is a definitely visible explosion. There is no sure sign in the appearance to distinguish such incomplete explosions.

(3) The degree of excess of oxygen makes no apparent difference to the completeness of combustion of the hydrogen.

To test whether the very slightly low results in (1) were due to incomplete combustion or to impurity in the hydrogen, some further mixtures of hydrogen with air were exploded. The gas, after explosion, was transferred to the combustion pipette, and the spiral maintained at red heat for a minute. In all cases, contractions were observed, corresponding to about 0·2–0·4 per cent. of the hydrogen (Table V).

TABLE V.

UNBURNT HYDROGEN AFTER EXPLOSION OF HYDROGEN-AIR MIXTURES.

Percentage composition of explosive mixture.		Percentage subsequent contraction in slow-combustion-pipette.	Percentage hydrogen unburnt (on total hydrogen).
Hydrogen.	Air.		
14	86	0·05	0·3
17	83	0·09	0·4
17	83	0·05	0·2
18·5	81·5	0·09	0·3
20	80	0·07	0·2
20·5	79·5	0·08	0·3

COMPLETENESS OF COMBUSTION IN THE EXPLOSION METHOD IN THE PRESENCE OF METHANE.—Misteli (*J. für Gasbeleuchtung*, 1905, **48**, 802) has stated that hydrogen cannot be accurately determined in mixtures of hydrogen with homologues of methane, since small quantities of the former escape combustion. To examine the magnitude of any such errors in the case of methane itself, various mixtures of hydrogen and methane with air were exploded in the larger apparatus.

After the gases had been measured subsequently to the explosion, they were transferred to the slow combustion pipette and the platinum wire heated at very dull redness for 1 minute. Whitaker (*Fuel*, 1925, **4**, 450) has shown that under these conditions small quantities of hydrogen are completely burnt, and methane unaffected. After the gases had been measured again, they were transferred again to the combustion pipette, and the wire heated at bright yellow heat for 2 minutes to burn any methane that remained.

Results are given in Table VI below.

TABLE VI.

COMPLETENESS OF EXPLOSION OF HYDROGEN, METHANE AND AIR MIXTURES.

Percentage composition of explosive mixture.			Percentage subsequent contraction in slow combustion pipette.		Percentage hydrogen unburnt. (on total hydrogen).
Methane.	Hydrogen.	Air.	1 min. dull red (*i.e.* unburnt H_2).	2 min. bright yellow (*i.e.* unburnt CH_4).	
0·5	11·3	88·2	0·08	0·07	0·5
2·1	10·5	87·4	0·05	—	0·3
3·2	10·5	86·3	<0·02	0·14	<0·2
4·9	5·7	89·4	<0·02	0·03	<0·2
5·6	7·0	87·4	0·02	0·06	0·2
5·8	7·1	87·9	0·03	0·03	0·3
6·4	6·1	87·5	0·04	0·10	0·4

The above results show that even when 6·5 per cent. of methane is present the amount of unburnt hydrogen is not greater than is the case when methane is absent.

Experiments with mixtures of methane and air in the absence of hydrogen showed similar proportions of unburnt methane to those above.

GENERAL SUMMARY.—(1) In the explosion method, errors caused by oxidation of nitrogen are negligible, provided the hydrogen in the explosive mixture does not exceed 20 per cent. For richer mixtures, this error is appreciable. In the slow combustion method, oxidation of nitrogen does occur, but to an extent negligible in gas analysis.

(2) The explosion method is always liable to small error, owing to incomplete oxidation of hydrogen. For mixtures containing between 10 per cent. and 20 per cent. of hydrogen this error is not more than 0·5 per cent. on the total hydrogen. For mixtures containing less than 10 per cent. of hydrogen such errors may be as much as 40 per cent. on the total hydrogen.

(3) Provided sufficient oxygen is present for the combustion of the hydrogen, the degree of excess of oxygen does not affect the completeness of combustion of the hydrogen.

(4) The presence of methane in any quantities suitable for explosion in gas analysis does not appreciably, if at all, increase the amount of unburnt hydrogen.

I wish to express my thanks to Mr. T. Carlton Sutton, M.Sc., F.Inst.P., for facilities and encouragement in carrying out this work.

RESEARCH DEPARTMENT, WOOLWICH.

Notes.

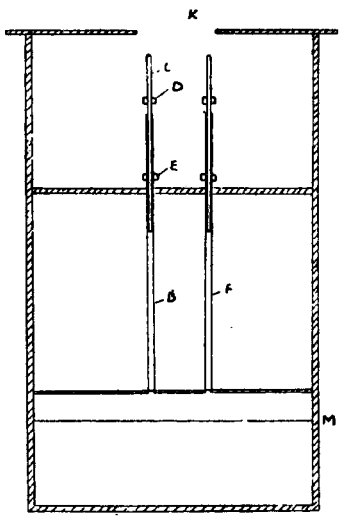
The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

AN EASILY CONSTRUCTED FORM OF MICRO COLORIMETER.

THE apparatus shown in the diagram was designed for the colorimetric determination of iron and manganese in the ash derived from the sap from fragments of plants. The quantity of liquid used in the colorimeter tube varied from 0·25 c.c. to 0·5 c.c. In the figure, B is a glass tube, 10 cm. long and 0·25 cm. in internal diameter. The lower end is closed by fusing a microscope coverslip over it in the following manner:—The coverslip is placed on a nickel crucible lid which has been well smoked in a benzene flame, powdered carbon is shaken round the edges of the coverslip, and a Rose crucible lid is placed over it. By this means the soot is prevented from burning away under the glass, so that it is not stained by the nickel when heated to redness by a Bunsen burner placed underneath. A thick brass wire which accurately fits the glass tube, and which has had its end made level with a very fine file, is inserted in the tube. Both the tube and the wire are passed into cork holders because they become hot by conduction. The wire is allowed to project

0·5 cm. from the end of the tube, and the ends of the glass and wire are blackened in a smoky flame. The wire is then withdrawn just inside the tube, which is heated more strongly, while at the same time the coverslip is heated to redness. The tube is now passed through the hole in the crucible lid on to the coverslip, and the wire is pushed down to keep the end true. The superfluous part of the coverslip can be broken away when cold.

A clear glass rod, C, slides in the tube, B, so that the depth of the liquid can be varied. The lower end of the rod is smooth, but the upper is ground with coarse carborundum powder to diffuse the light passing up. If this is not done



the apparent brightness varies with the angle of observation. D and E are rubber collars to cut out any light which has not passed through the glass rod. The rod is held in position by a piece of cotton carrying a small weight on the other end and passing over a kink in a horizontal wire (not shown). The other tube, F, is constructed in an exactly similar manner. The case containing the tubes is blackened on the inside and closed as far down as M, by a door. A small electric lamp with a sheet of tissue paper placed over it may be used below the tubes as a source of illumination, or a plain sheet of paper may be used with good daylight. Through the slit, K, in the roof the ends of the glass rods appear as luminous discs in a perfectly black field. The tubes should be placed as close together as possible, as this facilitates comparison. The liquid is introduced into the tubes by means of a glass tube drawn out at one end to a capillary. It is important to see that there are no air bubbles under the glass rod. The bubbles can be expelled by giving the end of the rod a smart tap while holding it, so that it cannot move much. The degree of accuracy obtainable is not much below that given by larger colorimeters.

The apparatus can be constructed cheaply, and several tubes can be prepared in a morning's work.

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CAMBRIDGE.

THE DETECTION AND DETERMINATION OF BENZOIC ACID.

THE detection and determination of small quantities of benzoic acid is still a matter of considerable difficulty. Although the reaction here described cannot be said to be specific for benzoic acid, yet, after examining a variety of foodstuffs, it has been found that only in rare instances would a definite colour be produced in the absence of benzoic acid.

The method depends upon the extraction of the benzoic acid, its nitration, reduction, and diazotisation. The diazo compound is decomposed in the warm solution, and then the excess nitrous acid reacts with the hydroxy body produced, and forms the nitroso or quinoxime derivative.

The following reagents are required:—(1) Acid mixture (2 of conc. sulphuric acid with 1 of fuming nitric acid); (2) 1 per cent. sodium nitrite solution; (3) strong ammonia solution; (4) zinc in strips.

A quantity of the sample containing 1–3 mgrms. of benzoic acid (generally about 10 grms.) is extracted with ether as usual. The well-washed ether is then extracted with about 2 c.c. of alkali solution. Mr. F. W. Richardson states that the evaporation of a soda solution of benzoic acid is attended by a loss of the acid, but that barium hydroxide solution fixes it.

After extraction with the alkali solution, the ether is washed with a minimum quantity of water, and the alkali and washings evaporated to dryness in a small porcelain dish. To the dried extract 2 c.c. of the acid mixture are added, and the dish heated on the steam bath for 5 minutes. The product is then washed into a Nessler glass, so that the total solution measures about 20 c.c. A strip of zinc is now added, and the reduction allowed to proceed for 10 minutes, the glass being placed on the top of the water oven. The zinc is then removed and 1 c.c. of the nitrite solution added. After 5 minutes, excess of ammonia is added, so that the zinc re-dissolves, and the solution is made up to 50 or 100 c.c.

A light to deep yellow coloration will be produced in the presence of benzoic acid. A quantity of benzoic acid approximately equal to that present in the sample should be treated in the same way and the colours matched. Of course, in the absence of the preservative the blank rarely remains colourless, but a little experience enables one to make the distinction.

J. C. HARRAL.

CITY AND COUNTY ANALYST'S LABORATORY,
BRADFORD.

THE PORPHYROXINE TEST FOR INDIAN OPIUM.

THIS test, according to Kanny Lall Dey (*Pharm. J.*, 1882, [iii], **12**, 397; *Allen's Commercial Organic Analysis*, 5th Ed., Vol. VII, pp. 714 and 724), can be used to differentiate Indian from Turkish or Smyrna opium. The test consists in making an aqueous extract of opium alkaline with ammonia or sodium carbonate, shaking out immediately with ether, evaporating to dryness, and warming the residue (rhoeadine?) with dilute hydrochloric acid, when a purple colour is developed.

Dey regarded the test as so characteristic of Indian opium that he used it in toxicological investigation (*loc. cit.*), since he obtained no such colour from Turkish or Smyrna opium.

A sample of opium recently seized in the Egyptian Custom House, packed in a tin box and labelled in Turkish as preserved fruit, in a consignment from Constantinople, was examined by this test, and the colour was readily obtained.

The evidence of the police was to the effect that the opium was a Turkish product, and therefore control experiments were tried on a sample of Smyrna opium supplied by The British Drug Houses, Ltd.

This sample also gave a positive reaction. Apparently the absence of the colour-producing constituent from Turkish opium is not general.

F. BAMFORD.

THE CHEMICAL LABORATORY,
MEDICO-LEGAL DEPT., CAIRO.

Notes from the Reports of Public Analysts.

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

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE YEAR 1929.

THE number of samples analysed during the year was 5455, of which 4838 were taken in connection with the Sale of Food and Drugs Act, corresponding to 495 samples per 100,000 persons. Of these, 344 were formal and 4494 informal samples; 274 (5·7 per cent.) were adulterated.

MILK.—During the month of October the milk from a herd of 26 cows was sampled each day over a period of 16 days on its arrival in Birmingham. On the day on which sampling began there was a drought, and this had been preceded by a similar drought. The conditions for feeding and watering the cattle were, therefore, very poor. The temperature varied from 37° to 65° F., and the climatic conditions were thus unfavourable to the cows. The results for solids-not-fat varied only from 8·5 to 8·9 per cent. for the morning milk, and from 8·5 to 8·6 per cent. for the evening milk. It will be noticed that the Ministry of Agriculture pamphlet, in describing the results for the herd which provided the variation of 0·87 per cent. of solids-not-fat between one day and the next, does not include any results below 8·5 per cent.

Place of Delivery.—Nine informal samples taken from a lorry delivering at a depôt were found to be deficient in solids-not-fat by 4·5 to 21 per cent., and several were also deficient in fat. On the following Sunday the consignment was sampled formally, and the deficiencies in solids-not-fat were found to vary from 3·5 to 22 per cent. The farmer accepted the usual offer to have his milkings inspected. There was nothing wrong with the cooler, but the milk, according to the farmer, was left out in the open overnight, so that it was possible for anyone to tamper with it, and it was found that the 38 cows were in good condition and yielded about 36½ gallons of milk. Four samples of the milk gave an average of 8·75 per cent. of solids-not-fat and 3·9 per cent. of fat, and proceedings were therefore instituted. At the hearing evidence was given that the milk had not been tampered with, but no evidence was available as to what happened while the milk was standing outside the dairy all night.

The technical defence was also raised that the depôt was not the place of delivery, on the ground that the milk was fetched by a private contractor employed by the wholesale dealer. It was maintained that the farm was, therefore, the place of delivery, but evidence for the prosecution showed that the farmer paid for the carriage of the milk from his farm to the depôt. The magistrates decided that the depôt was, in fact, the place of delivery, and fined the farmer £10 for one of the samples and £5 for each of the other 18 samples.

Nitrates in Milk.—Two informal samples contained 6 and 4·5 per cent. of added water, and four formal samples contained similar amounts of water, since they all contained nitrates, as well as being deficient in solids-not-fat. Samples taken from the individual cows on the farm were of very poor quality, but none contained nitrates.

In several other samples from different vendors the presence of nitrates raised the presumption that water had been added, although the amount of solids-not-fat was not less than 8·5 per cent.

LABELLING OF TINNED CREAM.—The label on a sample of tinned cream bore the words: "As with Devonshire Cream . . . the cream should be thinned before use." This would suggest that more fat than usual should be present, whereas the sample contained only 24·5 per cent., as against an average of about 50 per cent. for ordinary dairy cream, and 60 per cent. for Devonshire cream. The vendor was cautioned.

AMMONIATED TINCTURE OF QUININE.—This should contain 2·13 per cent. of quinine sulphate, 1·02 per cent. of ammonia, and 44·7 per cent. of alcohol. The formal sample contained only 1·09 per cent. of quinine sulphate, 0·75 per cent. of ammonia, and 32·9 per cent. of alcohol. The vendor was prosecuted and a fine of £2 was imposed.

See also ANALYST, 1929, **54**, 539; 1930, 38, 193.

Legal Notes.

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

WARRANTIES AS TO CATTLE CAKE.

G. C. DOBELL AND CO., LTD., *v.* BARBER AND GARRATT.

IN this case, heard before Mr. Justice Roche in the King's Bench Division, on May 21st, the plaintiffs, who were merchants, had bought from the defendants linseed cattle cake which had then been resold to dealers, who retailed it to farmers. The cattle cake contained castor seed and had made cattle seriously ill, and the plaintiffs brought the action to recover damages for breach of warranty.

The plaintiff's case was that the defendant's warranties to them under Sec. 2(2) of the Fertilisers and Feeding Stuffs Act, 1926, implied that the cake did not contain castor seed; and that, according to the fourth schedule of that Act, the cake was the residue from commercially pure expressed linseed. Alternatively, it was

claimed that the cake was warranted as reasonably fit food for cattle under Sec. 14 of the Sale of Goods Act.

The material words of the contract were:—

> The cake is sold *tel quel* in all respects, but . . . . . 's analysis, for which sellers accept no responsibility, is . . . castor free.

The defendant's case was that they sold only as agents, and were not liable as principals. They denied having sold the cake for use as cattle food, and denied the alleged warranties. The plaintiffs, they said, had taken samples before purchase and relied upon their own judgment.

Sec. 2(2) of the Fertilisers and Feeding Stuffs Act, 1926, provides that:

> On the sale for use as food for cattle of [linseed cake] there shall be implied, notwithstanding any contract or notice to the contrary, a warranty by the seller that the article is suitable to be used as such. . . .

By Sec. 24:

> This Act shall not apply to the sale of an article used as a . . . food for cattle . . . where the sale is in exercise of a statutory power to enforce a right or to satisfy a claim or lien, or where the sale is made by a sheriff. . . .

Mr. Porter, K.C., for the plaintiffs, submitted that warranties were implied by the Act, notwithstanding the wording of the contract. It must be assumed that both contracting parties had a knowledge of the Act. The defendants, therefore, warranted the cake as fit for cattle food, and the plaintiffs were justified in relying on that warranty.

Mr. du Parcq, K.C., for the defendants, contended that it was known to both parties that the cake was of Indian manufacture, and that such cake was open to suspicion. The defendants did not sell the cake for use as food for cattle, but sold to the plaintiffs as merchants who would not use the cake themselves, but would resell at a profit. The bank had a lien on the goods, and ordered the defendants to sell them; consequently, by Sec. 24, the Act did not apply.

Mr. Justice Roche, giving judgment, said that the plaintiffs had satisfied him that the defendants sold the cake for use as food for cattle. If the defendants' argument were accepted, it would mean that the only person who would be liable if the cake was unsatisfactory would be the small country dealer who ultimately sold it to the farmer. He decided that the large importers, who had the best opportunities for analysis, were within the section, and that there was a real sale by the defendants.

As regards Sec. 24, the bank did not want a forced sale, and employed the defendants to sell without disclosing that they were acting for the bank. He thought, therefore, that the sale was not within the meaning of the section. He held that the words of the section must be construed as covering a lien only when enforced by statutory power.

The plaintiffs were entitled to the declaration on the question of warranties, but, having regard to all the circumstances, he held that the plaintiffs were not entitled to recover as damages the sums which they themselves had been obliged to pay. They could only recover the difference between the value of the goods as they actually were at the time of the sale and their value as they ought to have been at that time.

CONTROL OF MINERAL WATERS AND THEIR SALTS UNDER THE FEDERAL FOOD AND DRUGS ACT, U.S.A.*

MINERAL waters are classed as both food and drugs under the Federal Food and Drugs Act, U.S.A., and failures to comply with the requirements are usually due to pollution with sewage and misleading claims as to therapeutic value, radioactivity, etc. It is required that all this class of water shall be free from sewage pollution, and shall show the presence of the *B. coli* group in not more than one out of five 10 c.c. portions collected from five separate containers. They shall also be of good quality when judged by the number of bacteria growing on gelatin at 20° C. or on agar at 37° C.; special significance is to be attributed to the presence of nitrite, to free ammonia in excess of 0·05 mgrm. per litre, and to an undue amount of organic matter. Mis-labelling is illegal.

W. P. S.

* J. W. Sale. (*Ind. Eng. Chem.*, 1930, **22**, 332–335.)

DAMAGE CAUSED BY FUMES AND SMOKE FROM CEMENT WORKS.

CHIVERS AND SONS, LTD., *v.* EASTWOODS CEMENT, LTD.

ON May 12th, Mr. Justice Bennett, in the Chancery Division, granted an injunction against the defendants to restrain them from working their factory so as to cause a nuisance by the discharge of smoke and fumes and the deposit of dust.

In his judgment Mr. Justice Bennett said that in 1927 the defendant company had begun to manufacture cement at works approximately half a mile to the south of the plaintiffs' fruit plantations, which were at a considerably higher level. The plaintiffs, in his view, had established beyond all reasonable doubt that noxious materials and gases emitted from the defendants' works had found their way on to the plaintiff's property and had caused visible damage to their fruit crops, and they had also proved that the damage they had sustained and were likely to sustain was serious, and not trifling in importance. The evidence showed that for the first time, in 1927, after the defendants had begun their operations, unpleasant smells and dirt were noticed on the fruit farms, and that in 1928 the raspberry crop which was then ripening, became scorched and shrivelled by dust, and a very substantial part of it was rendered useless. In May, 1929, when the plum and greengage blossom was in full bloom, the same thing happened. All the damage to both crops was done to the south sides of the trees. He was satisfied that considerable quantities of fine dust or impalpable powder were emitted from the chimney stacks of the defendants' kilns, and he had no doubt whatever that the damage to both crops was caused by this dust.

The defendants had not introduced any new method of getting rid of the dust which necessarily came from the kilns, and he had no alternative but to grant the injunction asked for, with costs, and an enquiry as to damage.

A stay of the injunction was allowed for 21 days, and, if notice of appeal was given within that period, there would be a further stay pending the hearing of the appeal, any intermediate damage to crops being included in the enquiry.

Department of Scientific and Industrial Research.

THE INVESTIGATION OF ATMOSPHERIC POLLUTION.*

REPORT ON OBSERVATIONS IN THE YEAR ENDING MARCH 31ST, 1928.

THIS, the fourteenth Annual Report, is the first made under the new arrangement whereby the Department of Scientific and Industrial Research is responsible for the work. It contains the Report of the Superintendent of Observations and four Appendices.

RESULTS OBTAINED BY THE DEPOSIT GAUGE.—Newcastle-on-Tyne shows for the third consecutive year the highest mean monthly deposit of carbonaceous matter, and Salford had an actual weight of tar deposit per sq. mile of 36 tons, and Burnley 140 tons of sulphates. The condition of the London atmosphere shows no improvement—in fact, rather the reverse—and taking the stations as a whole, there is little indication of improvement. Highest and lowest figures for the year, as metric tons per 100 sq. kilometres, were as follows:—*Tar*, Salford, 118; Huddersfield, Cooper Bridge, 2; *Carbonaceous matter*, Newcastle, City Road, 975; Birmingham, West Heath, 42; *Insoluble ash*, Newcastle, City Road, 1187; Leeds, Headingley, 83; *Soluble volatile matter*, Burnley, 701; London, Victoria Park, 69; *Soluble ash*, Burnley, 886; Rothampsted, 108; *Total solids*, Newcastle, City Road, 2973; Southport, Woodside Moss, 390; *Average Monthly Rainfall*, Rochdale Cemetery, 143 mm.; London, Golden Lane, 47 mm. The special tables for London and Glasgow indicate that in both cities the improvement in conditions noted in 1921–1922 ceased in that year, no further improvement being recorded, and whatever the causes, they appear to be common to both cities.

AUTOMATIC FILTER.—The curves for suspended sooty matter are plotted as usual, and indicate that the same general distribution holds good for all cities, that is, a comparatively clean period from midnight to 5 or 6 a.m., followed by a rapid rise of impurity. Where Sunday is included in the curve the peak for impurity shifts from 9 a.m. to 10 a.m.

JET DUST COUNTER.—The only complete set of observations is from the U.S.A. Weather Bureau, and these bring out that there is a relation between dust and sulphur content in the air.

MEASUREMENT OF DAYLIGHT.—A description is given of the examination into the strength of sunlight made at Salford in 1926–27, by exposing a solution of potassium iodide acidified with sulphuric acid in 2 oz. glass bottles in the presence of air and measuring the quantity of iodine liberated (*cf.* ANALYST, 1927, **52**, 641). The effect of the coal stoppage is clearly shown in the figures, and in the more normal year of 1927 the figures for the centre of the city are markedly higher than for the outlying districts, giving some idea of the effect of the smoke blanket.

Appendix I, by Dr. Owens, deals with the examination of the scale of shades for the automatic filter, and gives a method for calibrating any particular scale of shades from first principles, in the absence of a master scale. An apparatus of the revolving disc type is used, the discs being made of the same paper as the scales of shades. The error due to the limit of sensitiveness of the eyes in matching the

* Published February, 1930, pp. 67. Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3s. 6d. net.

automatic records with a scale of shades is also examined, and the given scale is so designed that physiological limits do not introduce any error into the readings greater than the divisions of the scale.

Appendix II, by Dr. Ashworth, is a Note on a Survey of Atmospheric Pollution in Rochdale.

Appendix III is a list of Observing Stations.

Appendix IV deals with methods in use for measuring atmospheric pollution, and is an extract from the "Note on the Investigation of Atmospheric Pollution," first published at the request of the standing Committee in July, 1928.

Pp. 27–67 comprise the General Deposit Tables.

D. G. H.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Separation and Determination of Solid Fatty Acids in Edible Fats. J. Grossfeld and A. Simmer. (*Z. Unters. Lebensm.*, 1930, **59**, 237–258.)—The fat (2·5 grms.) is saponified at the b.pt. for 10 minutes under a reflux condenser with 1 c.c. of 50 per cent. potassium hydroxide solution and 25 c.c. of 95 per cent. alcohol. In the case of oils with solid unsaturated fatty acids, 1 grm. is taken, and a 5 per cent. alcoholic solution of palmitic acid substituted for the alcohol. The boiling is continued after addition of 100 c.c. of a solution containing 50 grms. of lead acetate and 5 c.c. of 96 per cent. acetic acid in 1 litre of 80 per cent. alcohol (by volume), and 5 c.c. of 96 per cent. acetic acid until the precipitate has completely dissolved ; 20 c.c. of boiling water are added, and the mixture is allowed to cool slowly overnight to 22° C. The filtered precipitate is washed with 50 c.c. of 70 per cent. alcohol (by volume), and extracted with 3 c.c. of 96 per cent. acetic acid and 100 c.c. of the hot lead acetate solution. The hot solution is shaken with 15 c.c. of hot water, and the pure lead salts of the solid fatty acids separated by filtration on the following day, washed with alcohol as before, dissolved in 5 c.c. of 96 per cent. acetic acid, and 25 c.c. of warm 90 per cent. alcohol, and 5 c.c. of dilute nitric acid (sp. gr. 1·2) added. Warm water is added carefully, and the acids separated by heating at 98° C. until they form a clear layer on the surface ; they are then filtered from the cooled solution, washed till neutral and dried in the air, and finally in the oven. The iodine value is determined by back-titration with 0·1 *N* sodium thiosulphate solution (1 c.c. = 14·12 mgrms. or 0·5646 per cent. of iso-oleic acid), with starch as indicator, 15 minutes after the addition of 15 c.c. of 10 per cent. potassium iodide solution and 25 c.c. of Hanus iodine solution. The method gives higher results than that of Twitchell. With hardened arachis, cottonseed and marine and animal oils 13·3 to 33·8 per cent. of iso-oleic acid was found, but the results obtained are probably low on

account of the varying solubilities in alcohol of the lead salts. Bertram's vaccenic acid (*id.*, 1928, **55**, 179), an acid of the iso-oleic type, was found in beef fat (0·76 to 1·61 per cent.), mutton fat (0·99 to 1·84 per cent.), butter fat (1·13 to 4·69 per cent.) margarine fat (1·49 per cent.), and in lard (0·20 per cent.), and the fat from Blue-band margarine had an iso-oleic acid value of 17·89 per cent. Rape oil was shown to have an erucic acid content of 50·9 per cent., and an addition of 5 to 10 per cent. to linseed, arachis or sesame oils was detectable by the above method, other applications of which are also described. J. G.

Reducing Equivalents for some Rare Sugars as Determined by Colorimetric Methods. C. F. Poe and D. Klemme. (*J. Biol. Chem.*, 1930, **87**, 7–12.)—During the course of some research on the rarer sugars the reducing equivalents for these sugars could not be found in the literature, and it was, therefore, necessary to determine them with the use of glucose as a standard. The different colorimetric methods used were (1) the Lewis-Benedict method as modified by Willaman and Davison, (2) Folin-Wu, (3) Benedict copper method, first modification, (4) Folin, (5) Benedict copper method, second modification, (6) Folin, new, (7) Folin-Wu, new, (8) Sumner, and (9) Kingsbury. The glucose reducing equivalents have been checked for the common sugars with the older colorimetric methods. A table shows that the results of the authors agree with those of previous investigators, with the exception of a few cases. The glucose reducing equivalents have been determined for the more common sugars with the recently proposed colorimetric methods, *viz.* Folin, new, and Folin-Wu, new (*J. Biol. Chem.*, 1929, **82**, 83), Benedict, second modification (*J. Biol. Chem.*, 1928, **76**, 457; ANALYST, 1928, **53**, 230), and Kingsbury (*J. Biol. Chem.*, 1927, **75**, 241). With these methods the lowest equivalents are given by the new Folin method, except for laevulose. The glucose reducing equivalents have also been determined for a number of rare sugars by all of the satisfactory colorimetric methods. A table shows the results obtained with *d*-arabinose, cellobiose, fucose, glucoheptose, *β*-*d*-glucose, glucosamine and rhamnose. With these, as well as with the more common sugars, the copper methods give much lower results. Of the copper methods, the first modification of the Benedict method gives the highest equivalents, and the original Folin method gives the lowest. The results for the other methods are much higher, and are, in general, nearer unity. It is unusual to find such low results as are given by some of the rare sugars with the copper methods. There are a number of equivalents one-third and one-fourth the value of glucose. For fucose and rhamnose the authors find equivalents one-seventh that of glucose. The values for *β*-*d*-glucose are nearly unity, or the value of ordinary glucose. P. H. P.

Conversion of Dibenzal-Sorbitol into Hexa-acetyl Sorbitol. H. Jahr. (*Z. Unters. Lebensm.*, 1930, **59**, 285–288.)—For the detection of fruit juices in grape wine the sample is prepared in the manner described by Werder (ANALYST, 1929, **54**, 476) and by von der Heide and Hennig (*id.*, 422), and 50 mgrms. of the residue are dried in a vacuum desiccator, and placed in a tube (immersed in boiling water), together with 6 drops of benzaldehyde and 2 c.c. of *N* hydrochloric acid. After

15 minutes the liquid should be homogeneous, and is cooled, extracted with several 1 c.c. portions of ether, filtered, if necessary, into a dish, and evaporated with as much zinc oxide as the solution will dissolve. Acetic anhydride (0·5 c.c.) and a small piece of fused zinc chloride are added to the viscous residue, followed, afte 10 minutes on the water-bath, by 3 c.c. of water. The crystals which separat overnight are recrystallised from 4 c.c. of hot water. Hexa-acetyl sorbitol (m.pt 98° to 99° C.) forms prisms with a well-marked, obliquely-flattened edge, sometimes grouped in star clusters; hexa-acetyl mannitol (m.pt. 120° C.) forms rhombic prisms with triangular markings which have the appearance of diagonals.

J. G.

Constitution of Orotic Acid. M. Bachstez. (*Giorn. Chim. Ind. Appl.*, 1930, **12**, 174–178.)—This acid melts, with decomposition, at 345–346° C., and not, as has been stated, at 260° C., and is identical in all its properties and derivatives with uracil-6-carboxylic acid. When crystallised from water, orotic acid contains one molecule of water of crystallisation, which it loses at 130° C. It dissolves readily in potassium hydroxide or ammonia solution, subsequent addition of acetic acid precipitating, not the free acid, but its potassium or ammonium salt. The function of orotic acid in milk may be to furnish the developing organism with an important intermediate product for the formation of nucleins and to facilitate the biochemical synthesis of the purines. The physiological action of the acid is under investigation. T. H. P.

Hydrogen Cyanide in Lima Beans. II. Influence of Heat on the Poisonous Properties of the Beans. S. K. Hagen. (*Z. Unters. Lebensm.*, 1930, **59**, 211–216.)—The beans (50 grms.) are powdered, shaken for 3 hours with 400 c.c. of a citrate buffer (Sörensen) of *p*H 5·9, and the extract distilled with steam through a condenser, the end of which dips into 50 c.c. of 0·04 *N* sodium hydroxide solution. When 250 c.c. are obtained, 1 grm. of potassium iodide is added, and the solution titrated with 0·05 *N* silver nitrate solution (1 c.c. = 2·70 mgrms. HCN), with the assistance of a comparison solution titrated to the end-point. The error is 0·1 mgrm. of hydrogen cyanide, and amounts varying from 6·5 (Madagascar) to 53 (Rangoon) mgrms. per 100 grms. of beans were found. If the sample has previously been heated or treated with acid so as to destroy the enzyme, 25 grms. should be mixed with 25 grms. of an active meal of the same type before extraction, and allowance made for the hydrogen cyanide obtained from the latter. The enzyme is destroyed without affecting the glucoside content, by prolonged heating at 125° C., but is unaffected after 3 hours at 80° C. J. G.

Measurement of Colour in Red Wines. L. Roos. (*Ann. Falsif.*, 1930, **23**, 207–211.)—The intensity of the colour of red wines may be measured by comparison with a standard unit of colour conveniently made by dissolving 150 mgrms. of potassium permanganate and 300 mgrms. of dichromate in 1 litre of water. A quantity of this solution is placed in a test tube, and in another of equal diameter 1 c.c. of the wine to be examined, to which is added from a burette dilute acid

(5 grms. of sulphuric acid per litre) until the colour is matched, when the number of c.c. added plus 1 is the colour number of the wine. A good red table-wine should have a colour number of about 10. The method is based on one used by Hugues. D. G. H.

Red Colour of Oil in Preserved Sardine Tins. G. Hinard and M. Boury. (*Ann. Falsif.*, 1930, **23**, 216–218.)—At certain periods, generally towards the end of the manufacturing season, the oil in about 2 per cent. of the sardine boxes was found to be more or less tinted red, and in such boxes at least one sardine showed red-brown patches on the skin. A bacteriological examination of these marks showed nothing abnormal, and a chemical examination both of the packing oil and of the sardine oils led to the conclusion that under certain apparently accidental conditions sardine oil may show a red pigmentation. D. G. H.

Colour Reaction for Codeine and Dionine. G. De Haas. (*Pharm. Weekblad*, 1930, **67**, 508–510.)—The reaction for codeine given in Allen's *Commercial Organic Analysis* (5th Ed., p. 684) is best carried out by adding carefully, to a weak solution of codeine in a mineral acid, a dilute solution of bromine water till the solution is pale yellow in colour, and then an excess of ammonia. The rose colour produced distinguishes codeine from morphine, but not from dionine. Maximum colours are produced in 5 c.c. of solutions containing 1: 1000, 1: 3000 and 1: 6000 parts of codeine with 8, 5 and 1·5 c.c. of *N*/250 bromine water, respectively, and 1 c.c. of ammonia. Chlorine water gives inferior results, and sodium hydroxide cannot be used to replace ammonia. J. G.

Sterols of Ergot. M. C. Hart and F. W. Heyl. (*J. Amer. Chem. Soc.*, 1930, **52**, 2013–2015.)—A 0·13 per cent. yield of crude ergosterol was obtained from Spanish ergot by extraction with benzene, saponification of the extract, removal of the unsaponifiable fraction in ether, and precipitation with petroleum spirit. Crystallisation from alcohol, extraction with chloroform and further crystallisation from a mixture of alcohol and benzene yielded ergosterol in plates; m.pt. 163° to 164·5° C., $[\alpha]_D$ −123° (*cf.* Tanret, *Compt. rend.*, 1908, **147**, 75). Fungisterol (m.pt. 144° to 146° C., $[\alpha]_D$ −20°, acetate m.pt. 156° to 157° C.) was obtained from the combined filtrates from the above purification by concentration, several fractionations from ethyl acetate (the large top-fraction being discarded) and recrystallisation from alcohol. The results of Tanret (*loc. cit.*) were confirmed. A third sterol, $C_{27}H_{46}O$, (m.pt. 120° to 125° C.; $[\alpha]_D$ −2°; acetate, m.pt., 121° to 124° C., was obtained by acetylation of the bottom fraction from ethyl acetate and hydrolysis, and recrystallised from acetic anhydride and from alcohol. It gave a negative Rosenheim reaction, a positive Liebermann-Burchard reaction (incomplete saturation), and a yellow colour in the acid layer, turning slowly to orange in the Salkowski test. J. G.

Bacteriological.

Fermentation by Yeast Preparations. A. Harden and M. G. Macfarlane (*Biochem. J.*, 1930, **24**, 343–349.)—A living yeast may act in an excess of sugar solution producing 10 to 15 c.c. of carbon dioxide per 5 minutes for 2 grms. of pressed yeast; the fermentation is unaffected by the addition of phosphate except in high concentrations, when a slight inhibition may occur. The yeast juice prepared from such a yeast ferments at 1/20–1/40 of this rate; the addition of phosphate to the juice produces temporarily a rate of the same order as that of the original yeast, which falls to the normal as the phosphate becomes esterified, but can be maintained indefinitely in a suitable concentration of arsenate. It seemed of interest to determine at what point in the preparation of yeast juice, or by what reagents or treatment, this modified fermentation was produced. The preparation of yeast juice is usually carried out by grinding fresh pressed yeast with equal parts of silver sand and kieselguhr, and pressing out the ground mass after the addition of more kieselguhr in a hydraulic press. Investigation of the manner of preparation of the juice shows that at least 80 per cent. of the diminution in the rate of fermentation which occurs may be ascribed to the process of grinding, during which the yeast acquires the power of responding to phosphate. A further loss is incurred, during pressing, by the use of kieselguhr, which adsorbs active material. The effect of various reagents on the fermenting power of yeast is described; the ideal reagent sought after which would kill the cell so that it was incapable of growth but leave the fermentation rate unaffected, was not found. The conclusion is drawn that the treatments described affect mainly the mechanism of hexose-phosphatase action. An account is given of the preparation, by autolysis of dried baker's yeast, of an extract containing hexosephosphatase and accelerating the fermentation rate of zymin. P. H. P.

Biochemical.

Variations in the Zinc Content of Animals with Age. Influence of Milk Diet. G. Bertrand and Y. Beauzemont. (*Compt. rend.*, 1930, **190**, 1089–1092.)—Experiments on white rats gave results at variance with those of other authors, particularly Thompson, Marsh and Drinker (*Amer. J. Physiol.*, 1927, **80**, 64), who state that the mean normal concentration of zinc in white rats does not vary markedly at different ages. It was found that, although the mean weight of the rats increased from 5·76 grms. at one day to 13·6 grms. on the tenth day, the total zinc content per animal changed but very slightly (0·373 to 0·371 grm.), so that the percentage content decreased greatly. Gradual weaning, with administration of a diet of oats and moist bread, together with either fresh lucerne or beetroot, resulted in rapid recovery of the deficit in zinc, the proportion of which remained virtually constant at 3·5 mgrms. per 100 grms. of live weight, although at the end of the seventh month the body weight was twenty-one times that of

the newly born rat. It seems that milk, owing to its low zinc content, cannot for long satisfy the needs of a growing mammal. (See ANALYST, 1921, **46**, 244.)

T. H. P.

Arsenic Content of the Well Water of Choussy, at La Bourboule, and Fixation of the Arsenic by Organisms. R. Clogne, A. Courtois and Cazala. (*Compt. rend.*, 1930, **190**, 1133–1134.)—The arsenic content of this water, sampled several times during 1928 and 1929, varied from 5·8 to 6·5 mgrms. per litre. Batrachians, kept alive for 10 days in the water, which was renewed each day, were found to contain 0·00325 mgrm. of arsenic per grm. weight, whereas controls kept in ordinary water contained only 0·00188 mgrm. The corresponding figures obtained in experiments with the Choussy water which had been bottled for some time and with an arsenical solution of similar composition were 0·00273 and 0·002325 mgrm., respectively. T. H. P.

Detection of Nickel in the Cells of Plants. A. Martini. (*Mikrochemie*, 1930, **8**, 41–45.)—The formation of a complex caesium nickel compound, $Cs_2[Ni(SeO_3)_2]$, is used to detect nickel in microscope sections of plant material. When a drop of a saturated solution of sodium selenite is added to a drop of a 1 per cent. solution of a nickel salt on a microscope slide a white gelatinous precipitate of nickel selenite is formed. A very small amount of a saturated solution of caesium chloride is added on a gold thread and the mixture is stirred until the amorphous precipitate slowly disappears, and greenish white streaks appear on the slide. These are crystals of $Cs_2[Ni(SeO_3]_2$, and are seen under the microscope to be octahedral micro crystals which rapidly form other crystals of the first system. To confirm, the slide is washed with distilled water, and gently dried with a filter paper, when only the fine streaks remain. On adding a drop of a saturated solution of aluminium sulphate, caesium alum can be seen under the microscope. Nickel can also be shown to be present in the precipitate by repeating the reaction, washing and drying of the precipitate, and then adding an aqueous solution of dimethylglyoxime. On evaporating to dryness a red precipitate remains, consisting of small isochromic prisms of nickel dimethylglyoxime. Nickel was detected in varying amounts in the different parts of 80 different varieties of plants. J. W. B.

Composition of the Mixed Fatty Acids Present in the Glycerides of Cod-liver and certain other Fish-liver Oils. K. D. Guha, T. P. Hilditch and J. A. Lovern. (*Biochem. J.*, 1930, **24**, 266–290.)—Quantitative information has been collected as regards the composition of the mixed fatty acids present in specimens of Newfoundland, Scottish and Norwegian cod-liver oil, and also of the mixed fatty acids combined in the liver oils of coalfish (saith), hake, ling, skate, and dogfish taken off the north-eastern or north-western coasts of Scotland. The object was to collect data of an approximately quantitative kind with reference to the respective proportions of myristic, palmitic and stearic acids, and of unsaturated acids containing, respectively, 16, 18, 20 and 22 carbon atoms

in the molecule. The analytical methods used did not permit of the simultaneous determination of the individual unsaturated acids present in view of the complex mixtures of these generally present in the oils, but the records give an approximate expression of the average degree of unsaturation of each group, accompanied, where possible, by qualitative information as to the nature of the components. The analyses show no apparent correlation between the vitamin potencies of the oils studied and the composition of their fatty acids; in the cases examined the highest vitamin potency was observed in liver oils from the family Gadidae, but this may be a more or less fortuitous observation. The data obtained, in conjunction with a few other results of a similar nature already available, are classified from a biological standpoint in a table. The liver oils of the Gadidae and the flesh oils of the two members of the herring family stand apart from the rest in the approximate constancy of their general composition. Certain facts noted point to the synthesis of particular varieties of fatty compounds by specific classes of animals, but the general similarity in composition of the fatty acids of the livers, and in some cases the body-oils of many marine animals of diverse biological orders, suggests that fish and marine mammalia may derive a considerable proportion of their fats by direct assimilation. The polyethylenic acids of the C_{20} and C_{22} series (known only at one time as characteristic of fishes and marine mammals), were recently shown to be present in algae, and the fat of birds which feed on fish also contains these highly-unsaturated acids; thus, the determination of the origin (evidently marine in nature) of these unique highly unsaturated fatty acids is a problem of great interest which remains to be solved. So far as the present data go, there is a definite and close relation in the elasmobranch group between the character of the fat present and the amount and nature of the unsaponifiable matter. The results strengthen the conclusion of Hilditch and Houlbrooke (ANALYST, 1928, **53**, 246), that there is some connection between the absence of the polyethylenic C_{20} and C_{22} acids, so characteristic of most animal oils, and the presence of large proportions of squalene. The authors feel that at present no suggestion can be usefully offered to explain the genesis, much less a hypothetical transmutation, into one another, of either the polyethylenic acids, of squalene, or of cholesterol or other sterols, which are frequent components of the unsaponiable matter. From their fundamental differences in chemical structure it is difficult to imagine that they are mutually interconvertible by ordinary biochemical processes. It is perhaps more opportune to speculate whether different metabolic processes characteristic of specific organisms may not lead, according to circumstances, to the accumulation of differing kinds of organic compounds, and the disappearance of other forms which are further utilisable by the organism concerned.

P. H. P.

Fat-soluble Vitamins. XXVIII. Antirachitic Value of Cows' Milk as Modified by Exposure of the Cow to Sunlight and to Radiations from a Quartz Mercury Vapour Lamp. H. Steenbock, E. B. Hart, B. M. Risiing, C. A. Hoppert, S. Basherov, and G. C. Humphrey. (*J. Biol. Chem.*, 1930, **87**, 103–126.)—Previous work on goats by the authors has shown that, excluding

the feed as a possible factor in determining the antirachitic potency of milk, irradiation, at least with the goat, produced marked increase in the antirachitic properties of milk. Experiments which have now been carried out in the hope of improving cows' milk in a similar manner, show that daily exposure of cows to sunlight or artificially generated ultra-violet radiations has little, if any, effect on the antirachitic potency of milk. These experiments were carried out with Ayrshire and Holstein cows with coats for the most part unpigmented, and with the radiations falling on the head, back, or udders, the latter being almost free from hair. The radiation period in some cases was continued for an hour daily at 20 to 30 inches with Cooper Hewitt or Alpine Sun lamps. Rats were used as the test animals for both prophylactic and curative technique. The results stand in marked contrast to the earlier observations with goats. No improvement in milk or butter-fat secretion was observed. The well-recognised superior quality of summer-produced milk and butter-fat must, therefore, have its primary origin in other factors than sunlight acting directly upon the cow, and possibly, in the feed consumed by the cow. P. H. P.

Antimony Trichloride Colour Reaction for Vitamin *A*. II. Dilution Curve of Cod-liver Oil with Antimony Trichloride Reagent. E. R. Norris and A. E. Church. (*J. Biol. Chem.*, 1930, **87**, 139–146.)—In continuation of the work of Norris and Danielson (*J. Biol. Chem.*, 1929, **83**, 469; ANALYST, 1929, **54**, 612) and Norris and Church (*J. Biol. Chem.*, 1930, **85**, 477; ANALYST, 1930, **55**, 204), a few of the various types of dilution curves which may be obtained with antimony trichloride and fish liver oils have now been shown. There is apparently no uniformity in type of dilution curve with various oils, and, consequently, it is impossible to make any comparison as to the vitamin *A* potency of the oil where the colour produced is not a linear function of the amount of oil used. If the colour produced with any oil were a linear function of the vitamin present, and, therefore, of the amount of oil used, it would coincide with the tangent to the dilution curve at the origin. The relative potency of vitamin *A*, as shown by feeding experiments, agrees very closely with the relative colour-values of the tangent to the curve at the origin. A table shows the colours produced by chloroform solutions of 34 essential oils with antimony trichloride reagent; these oils were tested to determine if any would give a blue colour which might be mistaken for the blue produced by fish liver oils. Essential oils which were readily obtainable were used without regard to their value in flavouring fish oils. The essential oils are shown to give various shades of yellow, brown and red, with one green and one purple, but only one of the oils tested, cedar wood oil, was found to give an intense permanent blue, which had an absorption band with a maximum at 580$\mu\mu$. P. H. P.

The Antimony Trichloride Reaction of Cod-liver Oils. J. C. Drummond. (*J. Soc. Chem. Ind.*, 1930, **49**, 258T.)—A critical examination of the antimony trichloride reaction with cod-liver oils, and a comparison of results with those obtained from biological tests resulted in the conclusion that there was, in general, good agreement between the two methods of assay. The observation

by Hawk (*Science*, 1929, **69**, 200), that samples of cod-liver oils exposed to air and light sometimes show a more intense blue with the antimony trichloride test than those stored in the dark to preserve their vitamin content, could not be confirmed. D. G. H.

The Alleged Contamination of Carotene by Vitamin *A*. N. S. Capper. (*Biochem. J.*, 1930, **24**, 453–455.)—A good deal has been written recently concerning carotene and vitamin *A*, but the criticism, that even the purest samples of carotene might still contain traces of the familiar vitamin *A* of cod-liver oil, has remained incompletely answered. This problem has now been approached by a comparison of the ultra-violet absorption spectra of carotene and cod-liver oil concentrate. Cod-liver oil and its concentrates are characterised by an absorption band at 328$\mu\mu$, and this band is attributed with some confidence to the presence of vitamin *A*. Various workers have found that carotene can restore growth in rats receiving diets deficient in vitamin *A*. In an examination of carotene samples of varying degrees of purity, Dulière, Morton and Drummond have failed to detect this band at 328$\mu\mu$, and have suggested that the absorption of carotene in this region may be sufficiently dense to obscure completely any maximum due to the vitamin. The experiments now described lead to a different conclusion. They show that the intense vitamin *A* activity of carotene is not accompanied by the absorption band at 328$\mu\mu$, which is considered characteristic of the vitamin *A* of cod-liver oils. The absorption of carotene (m. pt. 178° C.) in this region is insufficiently intense to obscure the absorption at 328$\mu\mu$, which would be entailed by the presence of the cod-liver oil factor in an amount sufficient to account for the physiological activity of the pigment. Unless the close relation between the vitamin *A* activity of cod-liver oil and the 328$\mu\mu$ band is deceptive it is essential to assume that vitamin *A* can exist in at least two forms, only one of which absorbs strongly at 328$\mu\mu$, or that carotene behaves as provitamin *A*. P. H. P.

Vitamin *C* in Fresh and Canned Tomatoes. B. Clow and A. L. Martlatt. (*J. Agric. Res.*, 1930, **40**, 767–775.)—Guinea pigs were fed on a scurvy-producing ration, and the amount of recovery noted when tomato in various forms was given. The recovery dose of field-ripened tomatoes was found, under the conditions of experiment, to be 3 grms., and this was taken as the standard of comparison. Tomatoes canned by the cold pack method were as effective after 9 months' storage as the raw, but slightly less effective after 15 to 20 months, but canning by the open kettle method destroyed the vitamin to a marked extent, and even 4 grms. was not always a complete recovery dose. Green tomatoes (field or greenhouse matured) stored at 42° F. for 3 weeks, and then allowed to turn pink at 70° F., were unimpaired in vitamin *C* potency, but greenhouse tomatoes left to ripen on the plant were not quite so potent as field-ripened ones. Colouring of greenhouse tomatoes in an atmosphere of ethylene made little difference to the development of the vitamin, which increases in quantity with maturity, whether the tomatoes are on the plant or not. Raw, mature green tomatoes are less potent in vitamin *C* than those canned by the cold pack method, and practically no vitamin *C* is present in tomato pickles. D. G. H.

Colorimetric Method for the Assay of Rice for Anti-Beri-Beri-Vitamin Content. J. P. Spruyt. (*Chem. Weekblad*, 1930, **27**, 298–304.)—Ten grms. of whole rice are shaken mechanically for 20 hours with 5 grms. of decolorising charcoal (norit), 6 drops of toluene and 50 c.c. of a solution containing 1 per cent. of salicylic acid and 0·25 per cent. of sulphuric acid, the extract filtered, and 20 c.c. precipitated with 4 c.c. of 50 per cent. phosphotungstic acid. After 1 hour in a mixture of salt and ice and 12 hours at 30° C., 0·5 grm. of fine filter paper is added, and the whole centrifuged at about 3,000 turns per minute. The deposit is washed twice with 20 c.c. of the original extracting solution, transferred to a flask with hydrochloric acid (sp. gr. 1·1), and the brown-red colour produced on reduction by addition of zinc stabilised by means of a little stannous chloride. The solution is cooled, diluted to 250 c.c. and filtered, and the intensity of the colour measured in terms of the depth required to produce a match in a Duboscq colorimeter with a given depth (usually 100 mm.) of a standard solution having the same tint, and prepared from a suitable dye or from solutions of potassium dichromate, iodine and ferric thiocyanate. Allowance should be made for the blank on the reagents. In this way comparative values were obtained for 80 samples of rice, and comparison with the corresponding vitamin B_1 values (determined by animal experiments) showed that, in general, the method gives a better indication of the vitaminic activity than the phosphate content of the extract. For samples of low vitamin value all three methods are in approximate agreement. J. G.

Further Experiments on Cancer-Producing Substances. E. L. Kennaway. (*Biochem. J.*, 1930, **24**, 497–504.) **Spectra of Cancer-Producing Tars and Oils and of Related Substances. I. Hieger.** (*Biochem. J.*, 1930, **24**, 505–511.)—The carcinogenic factor in gas-works tar is known to be present in the higher-boiling fractions. A list is given, which was compiled by Kennaway (*J. Ind. Hyg.*, 1924, **5**, 462), of the compounds known to be present in tar with boiling points above 270° C., which temperature appeared to indicate roughly the boundary between the lower-boiling non-carcinogenic, and higher-boiling fractions; the results so far obtained by application of some of these compounds to mice are also given. Various materials have now been synthesised and painted on mice; the materials include tars, products of the action of aluminium chloride upon tetralin, acetylene, xylene, and other substances, compounds related to naphthalene, other hydrocarbons and quinones. The results show that carcinogenic products have been obtained by the action of aluminium chloride upon (*a*) acetylene, (*b*) xylene, (*c*) naphthalene, (*d*) naphthalene and bromobenzene, and (*e*) tetrahydronaphthalene (tetralin). Of these (*d*) and (*e*), under the conditions described, give the most active materials. It seems probable that the carcinogenic substance is produced by the heating in distillation, or at any rate is so increased in amount by this heating that it is able to produce tumours in mice. Hence the attempt to produce carcinogenic substances at body temperatures may not have been attained. Four cancers have been obtained in a series of 10 mice painted with a solution of a

fairly pure specimen of 1:2:7:8-dibenzanthracene. The last four of the 10 mice painted with impure 3'-methyl-1:2:5:6-dibenzanthracene have developed papillomata, and papillomata have been obtained in 1 mouse from the series of 10 painted with 1:2:5:6-dibenzanthracene. A number of new hydrocarbons have been synthesised and are now being tested on mice.

Work is described which deals with the application of optical methods to the identification of the cancer-producing agent present in tars and oils. The chemical separation of the cancer-producer will prove difficult, but it seems probable that the active agent is among the aromatic hydrocarbons with condensed rings. The fluorescence spectra of many cancer-producing substances show the same bands at wave-lengths 4000, 4180, 4400 Å. These bands are remarkably like those of the fluorescence spectrum of 1:2-benzanthracene, apart from their absolute wave-length. A study of the fluorescence spectra of a large number of condensed ring aromatic hydrocarbons shows that the spectrum is characteristic for closely related derivatives of a hydrocarbon. Absorption spectra in the ultra-violet also indicate, so far as the experiments have been carried, some connection between at least one powerfully cancer-producing material (*i.e.* the fraction boiling at 260 to 320°C./14 mm. from the mixture obtained by the action of aluminium chloride on commercial tetrahydronaphthalene) and 1:2-benzanthracene. P. H. P.

Organic Analysis.

Determination of the Hexabromide Value of Linseed Oil. F. Fritz. (*Chem. Ztg.*, 1930, **54**, 383.)—The following modification (see Steele and Washburn, ANALYST, 1920, **45**, 101) of the procedure for this determination is recommended. Not more than 1 grm. of the linseed oil fatty acids, weighed out into a Dewar vessel, is diluted with ether, cooled by addition of carbon dioxide snow, and brominated with a slight excess of bromine. The vessel is closed with a two-holed cork, carrying a glass tube which reaches nearly to the surface of the liquid and is connected with an efficient vacuum pump. The second hole serves for the supply of air, which passes beforehand through a roomy calcium chloride tower and, if necessary, through a large U-tube immersed in a bath of alcohol and solid carbon dioxide. If 0·5 grm. of the fatty acids is taken, the excess of bromine is removed in rather more than an hour. As little as 0·2 grm. of the acids may be used, but then, in order to avoid loss of hexabromide, ether saturated with hexabromostearic acid must be used for removing the other bromides. The cooled U-tube may be omitted if use is made, as separating agent, of absolute alcohol, which removes any moisture present. The hexabromide is separated and weighed as usual. With this procedure, Baltic and Plate linseed oils gave the hexabromide values of 57·8 and 50·5 respectively; the hexabromide was previously recrystallised from benzene and had m.pt. 179–180° C. T. H. P.

Determination of the Acetyl Value by Thermometric Titration. T. Somiya. (*J. Soc. Chem. Ind. Japan*, 1930, **33**, 140B.)—The solutions required are 3 *N* acetic anhydride and 3·1 *N* aniline, both dissolved in tetrachlorethane.

The former solution consists of a mixture of 300 c.c. of 92 per cent. commercial acetic anhydride, 280 c.c. of glacial acetic acid, and 420 c.c. of tetrachlorethane; the latter is prepared by mixing 200 c.c. of aniline and 500 c.c. of the same solvent. For the determination, a convenient quantity of the oil (in the case of castor oil 17 to 18 grms.) is heated with an equal amount of acetic anhydride in a vapour-tight pressure bottle for 2 hours at 140° C. An aliquot portion of the mixture is titrated with the aniline and acetic anhydride solutions (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 91B). The difference in the acetic anhydride found by titration before and after acetylation represents the amount of acetic anhydride combined with the oil, the result being calculated to millimoles of acetic anhydride for 1 grm. of oil or mgrms. of KOH for 1 grm. of acetylated oil. A blank determination should be carried out on the chemicals used. By this method the acetyl value of a sample of castor oil was found to be 143·5, as compared with 142·3 by the ordinary method. R. F. I.

Method for Determining the Degree of Purity of Cellulose Fibres. M. Freiberger. (*J. Soc. Dyers and Colourists*, 1930, **46**, 111–118.)—The amount of oxygen required to oxidise readily soluble reducing compounds present in modified cellulose is measured by means of an alkaline solution of potassium ferricyanide. A weighed quantity of about 0·2 grm. of the material is heated at 100° C. for ten minutes with 10 c.c. of *N*/200 potassium ferricyanide solution (1·65 grm. per litre) and 10 c.c. of 10 per cent. sodium hydroxide solution, then cooled, acidified with acetic acid, treated with a few crystals of potassium iodide and 10 c.c. of 5 per cent. zinc sulphate solution, and the liberated iodine titrated with *N*/200 thiosulphate solution. A control test is made at the same time with the reagents, but without the material. The thiosulphate solution is standardised against *N*/200 potassium iodate solution (0·1783 grm. per litre). The amount of ferricyanide reduced per 100 grms. of material is termed the "Ferricyanide Number," and the equivalent quantity of oxygen, calculated to 100,000 grms. of material, is called the "Oxygen Number." A well-bleached calico will have a "Ferricyanide Number" of about 1·66, and an "Oxygen Number" of 40·5, but with a calico containing much oxycellulose these values rise to 12·35 and 299, respectively. W. P. S.

The Decarboxylation of Pectin. F. V. Linggood. (*Biochem. J.*, 1930, **24**, 262–265.)—The pectins and hemicelluloses are normally to be found in association in the cell-wall, the relative amount of each being dependent on the condition of the tissue, *i.e.* whether lignified or non-lignified. The work of Candlin and Schryver (*Proc. Roy. Soc.*, 1928, B, **103**, 365) indicated the existence of an intimate relation between the two classes of substances, since pectin was shown to undergo decarboxylation under the influence of alkali, yielding *inter alia* a substance of the hemicellulose type, the yield of which amounted only to 12 to 20 per cent. of the pectin taken. The nature of the products which represented the major part of the pectin could not be determined. The sugars readily undergo profound changes in the presence of alkali, giving a variety of indefinite degradation products.

Therefore, if, as would seem possible, the pectin molecule yields sugars on decarboxylation, these would be destroyed immediately by the alkali present. Since the decarboxylation of pectin is a reaction likely to throw some light upon the question of the relationship between certain of the cell-wall substances, it is desirable to establish the nature of the substances other than hemicelluloses produced thereby, and thus it is necessary to use a decarboxylating reagent which will not tend to destroy these other products. The author has found that it is possible to produce decarboxylation of pectin by means of hot water under pressure, provided that the carbon dioxide evolved during the reaction is removed from the system. For the earlier experiments sodium pectate was used, but for the later ones this was abandoned and citrus pectin itself was used. The products obtained by such decarboxylation consist of an insoluble substance (about 20 per cent. of the pectin taken), probably a hemicellulose (mixed with a small quantity of undetermined matter), and one or more soluble products, possibly sugars. The hemicellulose-like substance has a uronic anhydride content of 6·2 per cent., and yields a mixture of sugars on hydrolysis. The investigation of the soluble products is not yet complete. Raising the temperature or prolonging the time of heating resulted in increased decarboxylation, but at temperatures above 153° C. charring was liable to occur. P. H. P.

Reaction for α-Naphthol. O. Carletti. (*Giorn. Chim. Ind. Appl.*, 1930, **12**, 178–179.)—Two c.c. of aqueous α-naphthol solution are treated in order, and with shaking, with 2 c.c. of saturated sodium bicarbonate solution, 0·5 c.c. of 10 per cent. potassium cyanide solution, and 1 c.c. of 1 per cent. copper sulphate solution. An intense reddish-violet coloration appears in presence of 0·001 grm. of α-naphthol, and the reaction is capable of detecting 0·00001 grm. of the substance. Under similar conditions, β-naphthol yields a faint yellow colour with green fluorescence. To detect traces of α-naphthol in the β-isomeride, 0·1 grm. of the latter is dissolved, with gentle heating, in 5 c.c. of saturated sodium bicarbonate solution, the liquid being cooled in running water, allowed to precipitate, and filtered. The filtrate, tested as above, will be pale yellow with green fluorescence if α-naphthol is absent, or reddish-violet if this is present. All the available samples of β-naphthol were found to contain α-naphthol when tested in this way, although they appeared free from this impurity when subjected to the test suggested in the Farmacopea Ufficiale (5th Edition, p. 357). T. H. P.

Determination of the *p*H value of Tan Liquors. L. Goldman. (*J. Inter. Soc. Leather Trades Chem.*, 1930, **14**, 211.)—Inconsistent results obtained in the determination of the *p*H value of tan liquors are caused by the reducing action of the hydrogen on certain oxidised compounds present in the tan liquors. Such inconsistencies can be avoided by modifying the technique in the following manner:—The platinum electrode is coated with palladium black by placing it, freshly cleaned, as the negative pole in a 1 per cent. solution of palladium chloride, and passing a current of 3 to 5 milliamps for 3 to 5 minutes. It is then washed,

placed as the negative pole in 5 per cent. sulphuric acid, with a current of 20 milliamps passing until the hydrogen bubbles off freely. It is again washed and held in position above the tan liquor. Hydrogen is passed for half-an-hour over the electrode and through the solution, but without the electrode being in contact with the solution. The hydrogen supply is stopped, the electrode immersed in the tan liquor, and an immediate reading taken. The electrode is withdrawn, hydrogen passed over it for a few minutes, again immersed, and a reading taken. This procedure is repeated till readings are constant. The *p*H values, as determined by the above method, agree with those observed for the same solution using the colorimetric dilution method of Thompson and Atkin (*J. Inter. Soc. Leather Trades Chem.*, 1929, **13**, 297). R. F. I.

Inorganic Analysis

Diethylbarbiturate Buffer. L. Michaelis. (*J. Biol. Chem.*, 1930, **87**, 33–35.)—In the series of buffers now used, there is no buffer system to cover the range around *p*H=8 with a sufficient reliability except the borate buffer of Sörensen, which has certain disadvantages in practical use. Recently Kolthoff found a dissociation constant of approximately 10^{-8} for diethylbarbituric acid (veronal). The author considered that this acid might be useful as a buffer for the wanted range, and found this to be the case. Veronal is recommended as a buffer covering a range from *p*H 6·8 to *p*H 9·6. It replaces not only the borate buffer, which is undesirable in many cases, but also duplicates a part of the phosphate buffer range, especially around the physiologically important *p*H 7·4. If 10·30 grms. of sodium diethylbarbiturate (veronal sodium) are dissolved in carbon dioxide-free water to a volume of 500 c.c., 10 c.c. of this solution titrated against 0·1 M. hydrochloric acid solution should use up accurately 10 c.c. of the acid to the turning point of methyl red. A table shows the *p*H values obtained when *n* c.c. of this stock solution (0·1 M. veronal sodium) are mixed with (10—*n*) c.c. of 0·1 M. hydrochloric acid solution. P. H. P.

Absorption of Carbon Monoxide by Cuprous Ammonium Salts. W. Gump and I. Ernst. (*Ind. Eng. Chem.*, 1930, **22**, 382–384.)—Cuprous ammonium lactate is a very satisfactory absorbent for carbon monoxide. A solution containing 13 grms. of cuprous oxide, 25 grms. of lactic acid, 85 c.c. of ammonia (sp. gr. 0·910) and 100 c.c. of water absorbs fifteen times its volume of carbon monoxide at 0° C., and this absorptive power remains the same after more than twenty regenerations in which the solution is heated at 80° C. to expel the carbon monoxide. Ammonia lost by evaporation must be replaced from time to time. W. P. S.

Colorimetric Determination of Orthophosphoric Acid. A. Dunajew. (*Z. anal. Chem.*, 1930, **80**, 252–263.)—Orthophosphoric acid may be determined colorimetrically, without separation, in presence of pyrophosphate, metaphosphate, phosphite, and hypophosphite, by a modification of Denigès' method (ANALYST,

1921, **46**, 24). To the solution in a 100 c.c. measuring-flask are added 25 c.c. of a solution containing 16 grms. of ammonium molybdate and 216 grms. of strong sulphuric acid per litre. The volume is made up to about 98 c.c. and the solution stirred; a few drops of stannous chloride solution are stirred in, and the volume adjusted. The tin solution must be added in slight excess; the intensity of the blue colour should not increase by another drop of the reagent. The matching of the tints is done 10 to 15 minutes after addition of the stannous chloride, and 2 to 3 minutes after addition of the further drop. The tin solution is made from 2 grms. of metal, 30 to 40 c.c. of strong hydrochloric acid, and 3 drops of 4 per cent. copper sulphate solution. When solution is complete the acid is completely expelled by evaporation on the water bath, the residue being dissolved in 10 c.c. of sulphuric acid (15 per cent. by volume). A 10 per cent. working solution is made by dilution with water, a one per cent. solution from 1 c.c. of strong tin solution and 5 c.c. of 15 per cent. sulphuric acid made up to 20 c.c.; a brown discoloration indicates deterioration. One to 5 drops of the 1 per cent. solution are added for 0·002 to 0·05 mgrm., 1 to 2 drops of 10 per cent. solution for 0·02 mgrm., and 5 to 7 drops of the same for 1 mgrm., of phosphorus. If oxidising substances (nitric acid, bromine, ferric iron) are present, correspondingly more stannous chloride is required. The method is stated to be useful in the study of the hydratation of meta- and pyrophosphates. W. R. S.

New Method for the Detection of Tin. H. Meissner. (*Z. anal. Chem.*, 1930, **80**, 247–252.)—The substance or solution to be tested is treated in a porcelain dish with a liberal amount of strong hydrochloric acid and a few small pieces of rod zinc. The mixture is at once stirred with a test tube containing cold water, and the immersed part then held in a colourless Bunsen burner flame. A vivid blue outer flame is evidence of the presence of tin. The test can be repeated several times with the same solution. A preliminary attempt is made to account for the reaction: it was ascertained that chloride ion must be present for the production of the blue colour. The substitution of sulphuric for hydrochloric acid causes the appearance of a reddish-violet flame. The present inference is that the formation of traces of tin hydride or a chlorine substitution product (*e.g.* $SnHCl_3$) is the cause of the coloration. W. R. S.

Determination of Small Quantities of Rubidium. E. Burkser, W. L. Milgewskaja, and R. W. Feldmann. (*Z. anal. Chem.*, 1930, **80**, 264–270.)—A fair separation of rubidium from potassium is possible, provided the proportion of rubidium is small, by the chlorostannate method (Moser and Ritschel, *Z. anal. Chem.*, 1927, **70**, 184). The procedure was re-investigated. The precipitant is a 40 per cent. solution of stannic chloride in absolute alcohol. The mixed chlorides are dissolved in a minimum of water, followed by 9 times its volume of a mixture (2: 1 by volume) of 96 per cent. alcohol and strong hydrochloric acid (37·2 per cent. HCl). The boiling solution—not more than 10 c.c.—is treated with 1 c.c. of the boiling-hot precipitant, the solution left to cool, and filtered next day

through a tared porous crucible; the precipitate is washed with absolute alcohol and dried at 110° C. to constant weight. The following results were obtained:

Exp.	Taken (grms.).	RbCl found.
1	0·0050 KCl + 0·0050 RbCl	0·0049
2	0·0250 ,, + 0·0050 ,,	0·0051
3	0·0250 ,, + 0·0050 ,,	0·0048
4	0·0500 ,, + 0·0050 ,,	0·0049
5	none 0·0100 ,,	0·0088

Separation of potassium chloride crystals (much more sparingly soluble in the alcoholic acid than rubidium chloride) took place only in Exp. 4; they were filtered off and washed with the alcoholic acid.

Further tests were made with synthetic solutions (1000 c.c.) containing large quantities of the chlorides of sodium, potassium, and magnesium, and sulphates of magnesium and calcium (see table below). Each solution was acidified with hydrochloric acid, boiled, and precipitated with barium chloride. The filtrate was treated with barium hydroxide followed by 10 per cent. sodium carbonate solution, which precipitated magnesium, calcium, and the excess barium, and the precipitate filtered off next day. The filtered solution was acidified and concentrated till sodium chloride crystallised out; the crystals were collected on a Büchner funnel, and the mother liquor again concentrated, etc., until only 20 c.c. remained; this was evaporated to dryness, and the residue dissolved in a minimum of water. The solution was diluted with 3 to 4 volumes of the alcoholic acid and left to stand overnight for the deposition of potassium chloride crystals. These were filtered off by suction and the filtrate evaporated to dryness. The residue was again dissolved in very little water, the alcoholic acid added, and the above operations repeated until no crystals of potassium chloride were deposited after one day's standing in a medium containing 9 parts of alcoholic acid and one of water. The solution was then submitted to the chlorostannate procedure. Three tests gave the following results (figures indicate grms.):

Exp.	NaCl +	KCl +	$MgCl_2$ +	$MgSO_4$ +	$CaSO_4$ +	RbCl.	RbCl found.
1	78·0	2·0	10·0	8·0	2·0	0·0100	0·0080
2	78·0	2·0	10·0	8·0	2·0	0·0050	0·0028
3	90·0	2·0	—	—	—	0·0010	0·0003

The authors conclude that the order of magnitude of the rubidium content of mixed salts is ascertainable even when it is as low as 0·001 per cent. The losses are ascribed to adsorption by the various precipitates. W. R. S.

Microchemical.

Semi-micro Combustion Determination of Nitrogen. W. M. Lauer and C. J. Sunde. (*Mikrochemie Pregl-Festschrift*, 1929, 235–242.)—The method is essentially the same as Pregl's method, but adapted for 20 mgrm. samples which may be weighed on an analytical balance sensitive to 0·05 mgrm. The combustion tube is 13 mm. in internal diameter and 45 cm. long, and is sealed to a tube of 5 mm. internal diameter and 8 cm. long. The permanent filling consists of

8–8·5 cm. of wire-form copper oxide, then a roll of reduced copper gauze 4 cm. long, and a layer of copper oxide 7 cm. long. Each is kept in place by a plug of asbestos. The sample is weighed into a porcelain boat, mixed with powdered copper oxide, and placed in the tube, and is followed by a roll of oxidised copper gauze. The absorption apparatus is similar to a Schiff azotometer, the carbon dioxide being absorbed by a 33 per cent. solution of potassium hydroxide. During the combustion the bubbles should pass at the rate of 8 in 10 seconds. Typical analyses of diphenyl urea gave percentages of nitrogen found 13·36, 13·04, 13·40 13·11, 13·22, as compared with the calculated 13·20 per cent. J. W. B.

Semi-micro Combustion Method for the Determination of Carbon and Hydrogen. W. M. Lauer and F. J. Dobrovolny. (*Mikrochemie Pregl-Festschrift*, 1929, 243–252.)—The method is a combination of the method of Wise (*J. Amer. Chem. Soc.*, 1917, **39**, 2055) and of Pregl with some modifications. Samples of 12 to 22 mgrms. are used, and weighings are carried out on a sensitive analytical balance. Pregl's pressure regulator, Mariotte flask and bubble counter are used, but the absorbing materials are potassium hydroxide and phosphorus pentoxide. The combustion tube is 1·2 cm. in internal diameter and 40 cm. long, and the tip is 2 cm. long, with an internal diameter of 3 mm. It is filled as in Wise's method. The rubber connections between the combustion tube and the absorption tubes are impregnated with vaseline, as in Pregl's method, and for the other connections artificially aged rubber tubing is used. The time taken for a complete determination is about 1 hour. The filling used was only suitable for substances containing carbon, hydrogen and oxygen, and for other substances must be slightly modified. A typical analysis (mannitol) showed percentages of hydrogen; found 7·6, 7·8 and calculated 7·75; carbon found, 39·7, 39·7, and calculated 39·54. J. W. B.

Micro-catalytic Detection of Platinum Metals. F. L. Hahn. (*Mikrochemie Pregl-Festschrift*, 1929, 77–80.)—A piece of asbestos paper, about 0·5 mm. thick, 2–3 cm. wide, and 6–8 cm. long, is taken, and in a moistened portion at one end a pointed lump is made by pressing a pointed glass rod on to the paper resting on a cork. The point of asbestos is heated to glowing in a Bunsen flame, and a drop of the test solution in a capillary thread is placed on the point which is made to glow again and then placed with its hollow side over a capillary through which pure (free from carbon dioxide) hydrogen is streaming. The asbestos glows or lights according to the concentration of the platinum metal. Using drops of 1 c.c. volume of known concentrations the content of platinum recognisable was 0·04γ. Iron, uranium, copper, molybdenum, nickel, etc., even in 1000 times greater concentration, do not interfere. More than 50 times the concentration of arsenic poisons the reaction. The smallest amount of palladium detectable is 0·01γ.

J. W. B.

Micro-detection of Thallium. A. J. Steenhauer. (*Mikrochemie Pregl-Festschrift*, 1929, 315–318.)—The tests were carried out on a slide and the crystals viewed through the microscope: (1) *Sodium thiosulphate* gives with thallium acetate

solution doubly refracting colourless crystals in cubes or cross-shaped rosettes. They are soluble in excess of sodium thiosulphate and in hot water. (2) *Ammonium dichromate* precipitates yellow-shaped aggregates of pointed crystals from nitric acid solutions of thallium compounds. (3) *Ammonium molybdate* gives from ammoniacal solutions colourless 6-sided thin leaves, showing interference colours with oblique light. (4) *Ammonium thiocyanate* precipitates doubly refracting prismatic crystals and needles. (5) *Mercury thiocyanate* gives fine polarising crystals which form larger ones on standing or rubbing with a platinum wire. (6) *Tartaric acid* precipitates polarising prisms. (7) *Picric acid* gives yellow needles and prisms. J. W. B.

Physical Methods, Apparatus, etc.

Ultra-violet Radiation of Essential Oils. C. P. Wimmer and M. H. Kennedy. (*Perf. Ess. Oil Record*, 1930, **21**, 163.)—Observations have been made on several hundred essential oils and allied substances, exposed in quartz test-tubes to the rays of a Hanovia quartz lamp fitted with a Corning glass filter transmitting ultra-violet radiations of 3900 to 2400 Å. None of the fluorescences noted are sufficiently characteristic to differentiate with certainty between a natural and a synthetic essential oil. The results do, however, assist in classifying these oils as regards their principal components, such as eugenol, citral, cineole, salicylate, anthranilate, etc. Moreover, terpene-containing lemon oil may be distinguished from terpene-free oil, hand-pressed from distilled citrus oils, eugenol from isoeugenol, methyleugenol from isoeugenol, methyleugenol from methyl-isoeugenol, and neroli oil from petitgrain oil. Fluorescence under the conditions named also indicates addition of petitgrain to other essential oils, such as lavender oil, or the presence of petroleum jelly or petroleum oil in, for instance, civet, and materially assists in the detection of adulterants such as terpinyl acetate, triacetin, etc., in essential oils when these are subjected to fractional distillation. T. H. P.

Use of Ultra-violet Rays in the Examination of Writing. H. Langenbruch. (*Chem. Ztg.*, 1930, **54**, 381–383.)—The detection of the order of application of superposed pen and pencil writing is discussed, reference being made to Mezger's work (*Chem. Ztg.*, 1929, **53**, 965, 985, 1006), in which the strong reflection of short-wave ultra-violet light by graphite is emphasised. With the help of reproductions of photographs, it is now shown, however, that definite conclusions are justifiable only when typical hindering of this reflection is observed, this denoting that the pencil writing has been written over with ink. The existence of the reflection, on the other hand, does not prove that the pencil marks are superposed on those of the ink. The structure of the pencil marks here comes into play, as this, with soft pencils, may be so fine and dense that superposed ink runs back and does not remain as a film, with the result that the reflection of the ultra-violet rays is not impeded. Moreover, the absorptive properties of the writing paper also affect the result.

As proof that the reflection by the graphite is prevented by an ink film is obtainable only when the ultra-violet photograph is taken at the proper angle to the direction of the strokes of the writing, it is necessary to take a series of photographs at different angles. T. H. P.

Photomicrography of Wool Fibres. J. Manley. (*J. Textile Inst.*, 1930, **21**, T231.)—The method given for photographing wool fibre aims at overcoming the difficulty of showing the structure at magnifications of 450 and 820. The best mounting medium is found to be a 3 per cent. solution of celluloid in amyl acetate, having a refractive index of 1·4049. The most suitable stain is either a 5 per cent. solution of acid fuchsin in 2 per cent. acetic acid or a saturated aqueous solution of picric acid, plus 2 per cent. of acetic acid. Fibres should be left in either stain for 1 hour at 37° C., then washed in methylated spirit and air-dried. The structure is shown up very well by means of oblique transmitted light at right angles to the length of the fibre. The sub-stage condenser should be achromatic, and should have an iris diaphragm which can be racked out of centre. If the diaphragm is centrally fixed, a stop must be introduced which may be moved to either side of the condenser. The source of light is a Pointolite. Dark-ground illumination is useless. Several photomicrographs are given, showing the effect of the different methods of mounting, staining and illumination. R. F. I.

Reviews.

THE CONDUCTIVITY OF SOLUTIONS AND THE MODERN DISSOCIATION THEORY. CECIL W. DAVIES, M.Sc., A.I.C. Pp. viii+204. London: Chapman & Hall, Ltd. 1930. Price 15s. net.

The impressions gained on opening this volume are well maintained on its closer examination. The publishers have done their work well; the book is excellently printed in clear type on smooth paper, and the reader allured to scan the whole volume at once, and then to settle down to reading the first chapter. Happily, the author's style is no less alluring, and the reader finds himself led on by clarity of expression and sequence of argument until he is obsessed with the subject, and these qualities persist throughout. The book, in both its theoretical and practical aspects, will appeal to the student and the experienced chemist alike. While the work is far from being rudimentary, it does begin at the beginning, and then launches out rapidly into deeper water, but never without sounding the depth, and thus the confidence and attention of the reader are held to the end.

The book is divided into three sections: (i) "Introductory"; dealing with the "Growth of the Ionic Dissociation Theory" and "The Theory of Inter-ionic Attraction"; (ii) "Methods and Results" (pp. 33–137), embodying twelve chapters;

(iii) "Some Applications and Consequences," the first chapter of which is devoted to "The Application of Conductivity Theory to Analysis." The titles of most of the twenty chapters are in terms familiar to all. The first appendix details "The Physical Constants of some Common Solvents," and the second gives a "Short Bibliography of Conductivity Measurements"; but the majority of the literary references of general interest are distributed throughout the text. There are twenty-two diagrammatic figures.

The book will be welcomed both by those familiar with the subject and by the analyst or works chemist who wishes to apply the principles of conductivity measurement to problems of technology. Those with little time for the subject will regret that the index is not more comprehensive. It occupies little more than three pages, and the majority of it is taken up with the names of workers. Numerous familiar expressions, for example, "conductivity measurements," "detector," "inter-ionic force," etc., fail to find a place, as also terms of occasional interest, such as "electrically-neutral doublets." Many practising chemists, as well as students and research workers, would appreciate a fourth section dealing with laboratory methods and equipment. This would increase greatly the usefulness of the work and might well be added without disturbing the present arrangement in a second edition, which we may anticipate with confidence.

S. JUDD LEWIS.

HANDBOOK OF CHEMICAL MICROSCOPY. Vol. I. By E. M. CHAMOT, Ph.D., and C. W. MASON, Ph.D. First edition. Pp. xiii+474, with 162 Figures. London: Chapman & Hall. 1930. Price 22s. 6d.

Since the days, not so very far distant, when the principal use of the microscope other than as a source of amusement, consisted of what was facetiously known as "diatom dotting," enormous advances have been made in the application of the instrument to problems in many branches of science. The range over which these applications have extended is evident from the present volume, which is based upon Chamot's "Elementary Chemical Microscopy," published some nine years ago, and reviewed in THE ANALYST (1922, **47**, 230). That work has been considerably extended in several directions, and much new matter has been included, recent developments in microscopical technique having necessitated complete revision and rewriting of the whole text.

The earlier chapters are devoted to the description, theory and practical manipulation of the microscope and its numerous accessories, the different types of the instrument and the various methods of illumination of transparent and opaque objects. These are followed by details of laboratory equipment, determination of the physical constants of fragments of material, ultramicroscopy, photomicrography, crystallographic methods as applied in mineralogy, the preparation of crystals, determination of refractive index, microscopic measurements and the quantitative analysis of heterogeneous mixtures. Interwoven among these are

many special methods and details of considerable value in many branches of microscopy.

Throughout the text there is abundant evidence that the authors are well acquainted with the apparatus and methods to which reference is made, and are capable of accurately and lucidly describing both the theoretical principles and the practical methods. To avoid overloading the volume, extensive references are given, throughout the text and in the appendix, to manuals, scientific journals, and other publications in which methods, etc., were originally described, the cosmopolitan nature of these indicating that but little of value has been missed. Since Volume II, dealing with chemical methods and inorganic qualitative analysis, is due to appear later, it is perhaps premature to mention that in the present volume no reference appears to be made to the enumeration and identification of mineral matters suspended in the air or other gases, the sampling of minute fragments of pigments from paintings, the identification of inks by the application of reagents to handwriting, nor to the separation of textile fibres by solution in various solvents.

Much care has been expended at all stages in the preparation of this work, and but little adverse criticism is therefore merited. Three minor typographic errors occur on pages **307**, **345** and **385**, where one finds "miscroscopes," "dessicant" and "*o*-Tuoluidene" respectively, and on page **174** reference is made to a cleaning preparation known as "Bon Ami," which, although perhaps familiar to American readers, does not appear to be recognised in London. Apart from these trifles, the volume is thoroughly reliable, and its value is greatly enhanced by the comprehensive and accurate index and by the copious references both to other pages of this volume and to the literature in general. It may be pointed out, however, that, although rarely met with, the page number as well as the figure number often saves considerable time when reference is made to an illustration in the same volume. Microscopists in general have reason to be grateful to the authors for the compilation of this work, which, in spite of its reasonable price, will prove of extreme value as an authoritative handbook and a trustworthy guide to many workers in the fields of physical, chemical and biological microscopy.

T. J. WARD.

THE CHEMISTRY OF THE COLLOIDAL STATE. By J. C. WARE, Sc.M., Ph.D. Pp. xiv+313. New York: J. Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1930. 18s. 6d. net.

Professor Ware in his preface emphasises the need for students to learn colloid chemistry, not only owing to its applications in all branches of industry, but also because "it is becoming more and more apparent that the student in all of the fields of chemistry is constantly requiring a greater knowledge of at least the fundamentals of the subject." For example, the student should certainly be familiar with elementary colloid chemistry when taking up his course in analytical chemistry, so that he should "know how to develop the most suitable type of precipitate" and avoid peptisation in washing his precipitates.

The author believes that, although excellent advanced texts are available, "the presentation for the beginner is not satisfactory," and "the presentation is not in keeping with modern tendencies." Such statements are too sweeping. Several elementary presentations are available and of the most authoritative standing. However, Professor Ware has added another to the list, and it will no doubt find a place on the beginner's shelves, as the matter is clearly presented and well illustrated.

The fourteen chapters are headed:—The Units of a Colloidal Solution; Sedimentation; Interfacial Phenomena (Non-Electrical); Turbidity and Colloidal Suspensions; Colloidal Suspensions and Colour; Motion in Colloidal Suspensions; The Electrical Character of Interfacial Phenomena; The Preparation of Substances in the Colloidal State; The Precipitation of Substances in the Colloidal State; Stabilisation or Protection of the Colloidal State; Water in Combination; Gels; Silica Gel and its Use in Adsorption; Catalysis by Contact Agents.

Chapter II on Sedimentation is a novel feature in elementary text-books, and has been well done. The student is given an intelligent and useful introduction to size-frequency analysis. Chapter III includes a discussion on adsorption. The legend to Fig. 25 (p. 57) states that "the amount (of solute) adsorbed is not related to the surface of the solid in contact with the solution, but to the weight of the solid." Surely the beginner will be misled by this. Again, p. 62, referring to the Freundlich adsorption isotherm, it is incorrect to say that "the formula would indicate that the material of the adsorbent does not affect adsorption." Incidentally, the reference to this equation, p. 59, is incomplete. On p. 67, the adsorption of gases by charcoal at 100° C. should read −100° C. On p. 83 occurs the statement: "The rate of adsorption of a solute from a solution is approximately expressed in the Freundlich isotherm." If "rate" is synonymous for "velocity" the statement should be deleted from the text.

Chapter XI deals with emulsions. Undue prominence is given to the Bancroft idea of the bending of an interfacial film because of inequality in surface tensions. Ramsden's alternative theory should have had mention. The explanation of the churning of cream to yield butter is woefully elementary (p. 235), and ignores the work of Rahn. There is a serious error (p. 237) in the statement that "certain deposits of crude oil consist of very persistent oil-in-water emulsions." The emulsions are definitely of the water-in-oil type. No discussion is given of froths or foams.

Certain industrial features are useful, such as the discussions of colloid mills, silica gel and catalysis. On the whole, the book is well written and the publishers' part deserves credit. A full subject index is given, but no authors' index. The price is reasonable.

WILLIAM CLAYTON.