

# THE ANALYST

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

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### Death.

With great regret we record the death of Mr. B. A. Burrell on July 10th.

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### Some Observations on the Washing of Gluten from Flour.

BY D. W. KENT-JONES, Ph.D., B.Sc., F.I.C., AND C. W. HERD, B.Sc., F.I.C.

*(Read at the Meeting, April 6, 1927.)*

THE determination of gluten in flour has long been recognised as a test which is open to much criticism. It is, however, essentially a simple test to perform, and one which millers are able to do for themselves. The gluten test, in the hands of an experienced operator, is certainly able to give useful information as to the quality of the flour. The test consists in making a dough, and then washing this dough under a stream of water, which removes the starch and most of the water-soluble bodies. The gluten is left behind in the hand, and from the weight of gluten, an approximate idea of the protein content of the flour can be obtained. Further, the skilled operator is able to gather much information from the character of the resulting gluten (stiff, flowy, elastic, snappy, etc.).

EFFECTS OF VARYING CONDITIONS ON THE TEST.—The test is essentially an empirical one, and the results depend largely upon the exact conditions of applying the test. This has been pointed out by a number of investigators. Arpin (1913) has pointed out that the composition and temperature of the water employed in washing influence the result. The French Official Method (Arpin, 1913) states that the water ought to contain about 100 mgrms. of total lime per litre, of which 80 to 90 mgrms. should be of the form of carbonate.

Wood (1907) has shown that small amounts of acids and salts can have important effects on the qualities of gluteins. Norton (1906) has given a full analysis

of crude gluten. His work has been confirmed by a number of investigators, and it has been shown that, generally speaking, dried gluten (dried in the water oven for 24 hours) contains 75 to 80 per cent. of proteins, the remainder being fat, starch, ash and fibre. Dill and Alsberg (1924) have critically investigated the subject of gluten washing and have recommended the use of a standard wash-water containing 0.1 per cent. of mixed phosphates, so that the solution has a  $P_H$  value of 6.8.

EXPERIMENTS ON DILL AND ALSBERG'S METHOD.—Cereal chemists find it necessary to report gluten contents to millers, and this work was undertaken to see whether the recommendation of Dill and Alsberg would be sufficient to ensure consistent results, when glutes are washed out by various operators in different parts of the country. A number of chemists, accustomed to gluten washing, were therefore asked to determine the gluten contents of a number of flours, using (1) their own tap water; (2) the special solution prepared according to Dill and Alsberg.

Most of them used the gluten washing-out method described by Kent-Jones (1924). The method is as follows:—Twenty grms. of flour are taken and made up into a dough with the requisite amount of water. This can be done conveniently by hand or by spatula. The dough is then placed in a small bowl of water and allowed to stand for one hour. A flow of water is then arranged, either from the tap or from a siphon in the case of the special solution, so that it runs at a constant speed of about 250 c.c. per minute. The dough is kneaded by hand under the flowing water; after a time, most of the starch has been washed away, and the gluten is left behind as a cohesive, coherent mass. In order to prevent the loss of small pieces of gluten, which tend to break off during the washing, a piece of fine silk is stretched immediately beneath the dough. The washing should occupy from start to finish exactly ten minutes. The pellet of gluten remaining in the hand is then placed on a dried and tared piece of paper and put in the water oven, at 98 to 99° C. for exactly 24 hours, when the weight of the dried gluten is obtained.

Eight flours were chosen:—"A" was a straight-run baking flour; "B" was a patent flour from the same mill (top 50 per cent.); "C" was a lower grade flour from the same mill (bottom 50 per cent.); "D" was as low a grade of flour as would be used commercially; "E" was a flour from the bottom of the mill and was much lower in grade than would be used commercially (it consists of flour which has been scraped from the bran); "F" was a straight-run flour made from Australian wheat; "G" was a straight-run flour made from Manitoba; and "H" a straight-run flour made from Barusso Plate.

Dried glutes have various colours, some being light-brown, some dark-brown, whilst some have a greyish tinge. No correlation between the colour of the gluten, and the grade of the flour or the method of washing out was noticed. The only safe observation to make is that the very low grade flours were generally of a lighter brown colour than the better grade flours, and also that sample "F" (the Australian) had a reddish-brown gluten with all operators.

Nine observers helped in this work. No. 1 was a chemist in an East Anglian mill. No. 2 was a chemist in an Irish mill. Nos. 3 and 4 were chemists in a Research Association, and they worked in the same laboratory (London district). No. 5 was a miller, who had received some instruction in cereal chemistry in the authors' laboratory, and the work was done in Manchester. Nos. 6 and 8 were the present authors. Nos. 7 and 9 were assistants in the authors' laboratory.

Table I indicates, however, that some observers get high, and some low results systematically, whether tap water (top line) or the special solution (second line) be used; the results are dependent on the idiosyncrasies of the operators and not on the solution used.

TABLE I.  
GLUTEN PERCENTAGES.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	Minimum.	Max.
"A"	11.70	13.70	13.20	12.70	11.61	11.93	10.94	11.60	10.01	10.01	13.70
	12.25	12.90	12.60	13.40	12.39	12.31	10.87	12.37	10.53	10.53	13.40
"B"	10.80	12.75	12.50	12.00	9.33	11.18	10.74	10.50	9.99	9.33	12.75
	11.02	12.60	12.20	12.20	11.81	11.83	10.46	11.57	10.48	10.46	12.60
"C"	12.55	14.55	14.00	13.60	12.45	13.81	12.04	12.41	11.81	11.81	14.55
	12.80	14.25	13.30	13.40	13.39	14.12	12.14	13.15	12.13	12.13	14.25
"D"	12.05	13.85	14.00	15.40	12.31	13.16	11.70	12.37	11.43	11.43	15.40
	12.45	13.50	13.10	13.00	12.93	13.35	11.48	12.60	11.96	11.48	13.50
"E"	17.70	19.30	19.60	19.40	17.97	18.73	16.80	17.43	16.75	16.75	19.60
	18.00	18.20	18.00	20.00	17.88	18.85	16.93	17.23	17.04	16.93	20.00
"F"	9.25	10.40	10.60	10.90	7.35	10.57	9.25	9.95	8.95	7.35	10.90
	9.55	10.45	9.90	10.60	10.15	10.23	9.41	9.85	8.86	8.86	10.60
"G"	12.50	13.85	12.90	13.50	—	13.20	12.02	12.71	11.60	11.60	13.85
	13.20	14.70	14.00	14.30	13.15	13.89	12.42	12.07	11.72	11.72	14.70
"H"	11.90	12.65	12.90	13.20	10.93	12.03	10.99	12.00	10.95	10.93	13.20
	11.60	13.00	12.00	12.90	12.20	13.09	10.96	13.28	10.98	10.96	13.28

*Nitrogen in the Glutens.*—All the glutens were then analysed for nitrogen. The nitrogen results were multiplied by 5.7, the accepted factor for conversion into protein. From these results the figures given in Table II were calculated. Table II thus shows the percentage of protein ( $N \times 5.7$ ) in the glutens, which had all been dried to constant weight. It will be seen that about 70 to 80 per cent. of dried gluten is protein, a figure in agreement with that of Norton (1906). It

TABLE II.

NITROGEN PERCENTAGES IN THE GLUTENS.

	1.	2.	3.	4.	5.	6.	7 <sub>2</sub>	8.	9.
"A"	—	68.80	71.99	70.00	86.60	79.00	81.80	78.77	83.79
	77.41	69.20	74.21	71.02	78.77	78.77	85.39	79.40	84.19
"B"	81.23	69.83	70.22	72.62	81.80	81.00	84.59	82.99	84.02
	81.00	70.40	75.01	74.61	79.57	75.81	84.99	79.97	84.76
"C"	77.98	69.83	71.25	75.98	75.81	74.78	81.97	77.98	81.80
	78.83	65.61	77.98	77.58	76.78	75.01	83.62	79.00	82.59
"D"	80.77	70.00	70.22	66.63	81.39	64.81	82.37	79.23	81.57
	73.59	70.17	76.38	76.84	77.80	75.01	80.20	76.30	81.00
"E"	71.00	67.83	70.22	69.43	76.38	65.04	73.20	75.58	75.81
	74.39	70.40	74.78	71.25	75.24	71.82	77.98	77.24	75.41
"F"	77.00	69.20	68.40	71.59	79.23	73.81	80.43	75.58	81.23
	—	71.99	77.01	75.58	75.24	75.25	79.57	76.30	78.77
"G"	—	70.79	77.01	77.98	—	78.32	83.79	82.99	79.23
	—	67.43	77.80	77.58	81.57	78.20	82.88	79.40	79.57
"H"	—	69.83	71.82	72.11	81.17	78.20	81.97	79.80	79.57
	80.77	69.03	78.77	76.21	78.95	70.22	84.82	78.32	81.57

is interesting to note that operators Nos. 3 and 4, working in the same laboratory, obtained similar results which are, with the exception of No. 2, below those of the other operators. The highest results are those obtained by operators Nos. 5 and 7. Out of the sixty-eight comparisons given, there are forty in which the protein percentage in the gluten is higher with the special solution and only twenty-eight in which it is higher with the tap water.

*Ratio of Gluten to Nitrogen.*—Table III gives some interesting results on the gluten-nitrogen ratios. It is very useful in cereal laboratories to check nitrogen and gluten results. The ratios given in Table III were obtained by comparing the dried glutes given in Table I with the nitrogen contents of the flours; the nitrogen contents given are the averages of two or three estimations. It will be seen from Table III that the gluten-nitrogen ratio depends entirely on the personal manipu-

TABLE III.

	GLUTEN: NITROGEN RATIOS.									Nitrogen content of flour. Per Cent.
	1.	2.	3.	4.	5.	6.	7.	8.	9.	
"A"	6.2	7.2	6.9	6.7	6.1	6.3	5.8	6.1	5.3	1.90
	6.4	6.8	6.6	7.1	6.5	6.5	5.7	6.5	5.5	
"B"	6.1	7.2	7.0	6.8	5.3	6.3	6.0	6.0	5.3	1.78
	6.2	7.1	6.9	6.9	6.6	6.6	5.9	6.5	5.9	
"C"	6.1	7.1	6.9	6.7	6.1	6.7	6.0	6.1	5.8	2.04
	6.3	7.0	6.5	6.6	6.6	6.9	6.0	6.5	6.0	
"D"	6.2	7.1	7.2	8.0	6.3	6.8	6.0	6.3	6.0	1.95
	6.4	7.0	6.7	6.8	6.6	6.8	5.9	6.5	6.1	
"E"	6.3	7.0	7.0	7.0	6.4	6.7	6.0	6.2	6.0	2.79
	6.45	6.5	6.45	7.2	6.4	6.8	6.1	6.2	6.1	
"F"	6.3	7.1	7.2	7.5	5.0	7.2	6.3	6.8	6.1	1.46
	6.5	7.2	6.8	7.2	7.0	7.0	6.4	6.7	6.1	
"G"	6.3	6.9	6.5	6.8	—	6.6	6.0	6.4	5.8	2.00
	6.6	7.4	7.0	7.2	6.6	6.9	6.2	6.0	5.9	
"H"	6.4	6.8	7.0	7.1	5.9	6.5	5.9	6.4	5.9	1.86
	6.2	7.0	6.5	6.9	6.6	7.0	5.9	7.1	5.9	
Average	6.25	7.0	7.0	7.1	5.9	6.6	6.0	6.3	5.8	
	6.4	7.0	6.7	7.0	6.6	6.8	6.0	6.5	5.9	

lation of the operator. It will be clearly seen, from the averages given at the foot of Table III, that there are usually only slight differences between the tap waters and the special solutions, but that there are very big differences between the various operators. In the authors' laboratory, therefore, this personal factor has been determined, and it is possible to check, with approximate accuracy, the dried gluten content with the nitrogen in the case of each individual observer. The gluten-nitrogen ratio for each operator is fairly constant, the kind of water used making no difference. It was thought that the various operators might have worked at different temperatures, and that this might have been one of the main causes of the different gluten-nitrogen ratios reported. All the operators reported the temperatures at which the gluten washings were carried out, and the total range was from 12° to 19° C. The gluten content of a flour at 12° and at 26° C. was determined, but the difference was not important. An increase of 0.03 per cent. was obtained for each degree rise in temperature. This is in fair agreement with

the figure calculated from the data of Arpin (1913), which was 0.024 per cent. for each degree centigrade. In one instance the dried gluten content of a flour at 12° C. was 10.61 per cent., whilst at 26° C. it gave 11.05 per cent.

Although there is obviously some personal factor which causes the difference in the results obtained between various operators, it was not possible to detect what this was. The effect of removing the starch in the washing out of gluten quickly and slowly was investigated. In a typical instance the majority of the starch was washed out slowly, *i.e.* in six minutes, the washing then being continued for the normal ten minutes. This gave a result of 10.85 per cent. Most operators remove the majority of the starch in four minutes. This more normal procedure gave a result of 10.61 per cent.

CONCLUSIONS.—It has been shown that the use of a special solution, such as the one suggested by Dill and Alsberg, does not eliminate the errors inherent in gluten determinations. Even when apparently the same method is used by various operators, *i.e.* the same amount of washing water used, and the same procedure followed, there are personal differences in the manipulations of the dough and gluten, which cause big variations in the result. It is this untraced personal factor that leads to discrepancies in the results from various operators. It has been shown, however, that each operator gets essentially consistent results, which means that the ratio between the nitrogen of the flour and the dried gluten is approximately constant for each operator.

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## A Numerical Expression for the Colour of Flour.

BY D. W. KENT-JONES, Ph.D., B.Sc., F.I.C., AND C. W. HERD, B.Sc., F.I.C.

(Read at the Meeting, April 6, 1927.)

THE colour of flour is a matter of the greatest importance in the milling industry. There is a great public demand for clean, bright and white flour. It is very difficult to judge the colour of flour. The actual granularity of the flour may have an effect, as the large granules cast shadows which register grey hues, unless regular illumination is ensured. Besides the darkening effect of traces of dark and foreign matters, there are, however, two main factors which determine the colour of flour. There is, firstly, the effect due to the carotin, the yellow pigment of

flour. This has been studied by a number of investigators particularly Willstätter and Mieg (1907) and by Monier-Williams (1912). The bleaching of flour is normally due to the oxidation of this yellow pigment to a colourless body. Chlorine is said to bleach by the formation of a colourless chlorine additive compound of carotin. Secondly, there is the effect due to the minute particles of bran, which are always present and which contain a reddish-brown pigment. It is not feasible to bleach this reddish-brown pigment. The ordinary bleaching agents for flour have little or no effect. Sulphur dioxide has a distinct bleaching effect, but cannot be used as it is deleterious to the baking property of the flour. Palmer (1924) states that this reddish-brown pigment is xanthophyll.

PREVIOUS METHODS OF COLOUR DETERMINATION.—Jago (1911) has given the results of a large number of colour determinations on flour obtained by means of the Lovibond tintometer. It is generally admitted that the Lovibond tintometer is very unsatisfactory for flour work, as personal judgment has too great an influence. The differences between the colours of flours are comparatively slight; they are not like the differences in the colours of beers. In the milling trade what is known as the Pékar test is employed. In this, compressed slabs of flour, which are placed side by side, are dipped into water and then allowed to dry. The colour of the flour is darkened as the result of the oxydase present. The test is really only useful for making immediate comparisons between flours, as the colours cannot be carried in the mind. Also, from the authors' experience, the Pékar test does not correspond exactly with the colour of the resulting loaf. Realising that there are at least two main colour factors in flours, some millers prefer to examine the flours through blue glass, which helps to eliminate the yellow effect of the carotin and merely records, in a rough way, the effect of the reddish-brown pigment.

It is customary in the United States to determine the gasoline value of flour. This is described in the *Methods of Analysis of the Association of Official Agricultural Chemists* (page 230, 1925 edition). This method gives very good results for the determination of the intensity of the yellow colour caused by the carotin. It does not, however, take into account the presence of the even more important colouring matter, the reddish-brown pigment from the bran particles.

In the North of England particularly, the matter of flour colour is of the greatest importance. Bakers in Lancashire and Yorkshire are prepared to pay fancy prices for patent flour. It would be very difficult to sell flour to Lancashire and Yorkshire bakers which was made from a large proportion of Durum wheat without bleaching, as the resulting flour would be too highly coloured. Further, they demand a flour which is as deficient as possible, not only in the yellow carotin, but also in the reddish-brown pigment.

SEPARATE MEASUREMENT OF THE TWO COLOUR FACTORS.—We thought that it might be possible to obtain two definite numerical expressions for the colour factors in flour by the use of two solvents. The first solvent should dissolve out the reddish-brown pigment, and the second one should deal purely with the yellow

effect of the carotin. The American gasoline colour figure was found to be quite satisfactory for the second of these, but some trouble was encountered in finding a satisfactory and reliable solvent for the more important reddish-brown colouring matter. In the course of some experiments on the determination of glutenin by the Blish and Sandstedt (1925) method, it was noticed that alkaline methyl alcohol has a very useful solvent action in this respect. As the result of many hundreds of trials, we are satisfied that the procedure given below will determine with accuracy the intensity of this reddish-brown colour. A combination of these two colour determinations will, therefore, give full information on the colour of any particular flour.

**THE COLORIMETER.**—In the first instance a Kober colorimeter was employed, but it was not sufficiently sensitive, and unsatisfactory duplicate results were obtained. An apparatus was then made for us by Messrs. Gallenkamp & Co., Ltd., whereby yellow light from an opaque "fullolite" bulb, F, with switch, G, is filtered through Special blue glass, which gives standard daylight. This is reflected by the plate, E, through flat-bottomed Nessler glasses, CC, which are viewed from above through the single eyepiece, A, beneath which are the

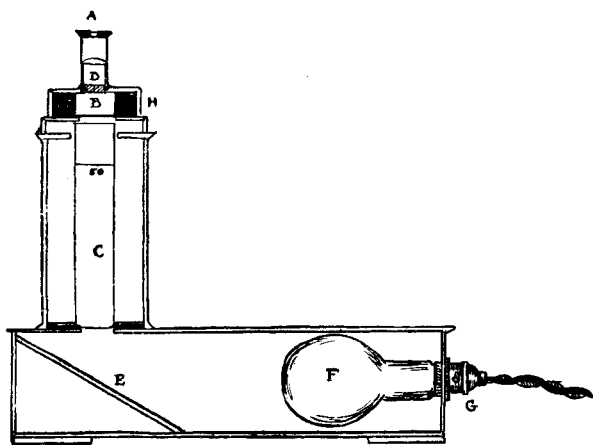


Fig. 1. Side elevation.

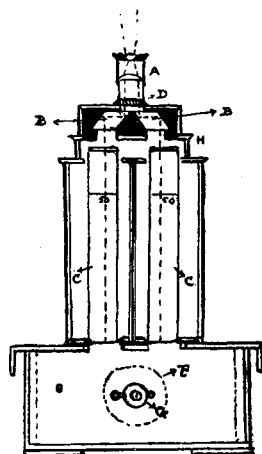


Fig. 2. Front elevation.

prisms, BB, for producing a split field. Between the eyepiece and prisms is the daylight filter, D, for which we prefer a diaspec lens. The small box, H, is hinged and will fit closely over the Nessler glasses. The inside of the large box (approximately 10" × 5" × 5") is painted white to ensure equal dispersion of light.

**EXTRACTION OF THE REDDISH-BROWN PIGMENT BY ALKALINE METHYL ALCOHOL.**—This extraction was standardised as follows:—Twenty grms. of flour are introduced into a wide-mouthed glass-stoppered 8 oz. bottle, and 50 c.c. of distilled water added; the stopper is inserted and the bottle shaken to effect a

complete mixing of the flour and water; 5 c.c. of a normal sodium hydroxide solution are then added, and the bottle is again vigorously shaken, and then allowed to stand for one hour with intermittent shaking, say, at approximately every ten minutes. At the end of the hour, 100 c.c. of methyl alcohol are added, and the whole shaken thoroughly overnight (16 hours). In the morning the supernatant liquid is decanted into a beaker, and the glutenin is precipitated by the addition of N/5 hydrochloric acid. Blish and Sandstedt have shown, that the glutenin is completely precipitated at a  $P_H$  of 6.4, and for the purpose of this colour test it is necessary to use the indicator brom-thymol blue externally; this can be done equally effectively with a spotting tile or by taking out 2 to 3 c.c. in a small test tube and adding the indicator, the change being the formation of a light-olive colour. The precipitated glutenin is allowed to stand for one hour, and then is centrifuged, the glutenin being thrown to the bottom as a compact disc. The supernatant liquid is filtered off through a No. 5 Whatman paper into a clean, dry beaker. Fifty c.c. of this filtrate are taken, and 1 c.c. of caustic soda solution is added; this is sufficient to render the methyl alcohol mixture distinctly alkaline, and the colour of the pigment, which is destroyed in acid solution, is reproduced. This 51 c.c. of solution is then introduced into the Nessler glass for the colorimeter. The details of the preparation of the standard solution for matching this extract are given under the paragraph describing the making of a determination.

**EXTRACTION OF THE CARROTIN.**—The method used is very similar to the one given in the Association of Official Agricultural Chemists Methods of Analysis:—Twenty grms. of flour are weighed into a wide-mouthed glass-stoppered 8 oz. bottle, and 100 c.c. of standard grade petrol is added (Pratt's Aviation spirit is used for this purpose by the authors). The bottle is stoppered tightly and contents thoroughly mixed and shaken periodically for about 15 minutes. It is then allowed to stand for 16 hours (overnight is a convenient period); at the end of this period the contents are re-shaken, and after a few minutes standing to allow most of the flour to settle, the moderately clear petrol extract is poured off on to a No. 5 Whatman filter paper, and filtered into a dry conical flask. The funnel is kept covered by a watch glass during the filtration in order to prevent evaporation, and it is usually found necessary to re-filter the first few c.c. of the filtrate. When sufficient of the filtrate has been collected, 50 c.c. are transferred to the Nessler glass, which is then inserted in the colorimeter. The details of the preparation of the standard solution for matching this extract are given in the following paragraph.

**METHOD OF DETERMINATION.**—The prism box, H, is turned on its hinges so that the Nessler glasses can be inserted. The Nessler glass containing the extract is placed into the left hand recess (the left hand recess has been chosen quite arbitrarily by us). To the other Nessler glass are added about 40 c.c. of water and a trial number of c.c. of the particular standard colour solution. This is then placed in the right hand recess. The prism box is now closed down, and the single field is viewed through the eyepiece A. A very good comparison is obtained. It is



customary to use too little of the standard colour solution at first, so that the prism box is again turned on its hinges, the Nessler glass removed, and a further quantity of standard colour solution added. It is then replaced and a fresh observation made. These operations are repeated until a very close match is obtained. For accuracy the final comparison can be made in three stages:— (1) When the standard is just too light; (2) when in the opinion of the observer the depth of the solutions are almost exactly the same; (3) when the standard solution is slightly too deep; and by this means a sharp comparison is obtained.

The standard solutions suggested have been carefully designed so that the tints of the extracts and the standards should be the same. The comparison with the split field is therefore easy to make, as it is purely a comparison of depth of colour. The personal factor is found to be largely eliminated in this way. This point has been carefully tested by getting observations made independently by several people.

*Standard Solutions.*—The following are the standard solutions adopted:—

- (1) *Standard Solution for Alkaline Methyl Alcohol.*—Five c.c. of 0.5 per cent. potassium chromate solution, and 2.0 c.c. of 10 per cent. anhydrous cobalt nitrate solution. This is made up to 100 c.c. with distilled water.
- (2) *Standard Solution for the Carrotin Extract.*—Ten c.c. of 0.5 per cent. potassium chromate solution, and 1.5 c.c. of 10 per cent. anhydrous cobalt nitrate solution. This is made up to 100 c.c. with distilled water.

The 0.5 per cent. potassium chromate solution and the 10 per cent. cobalt nitrate solution keep well, but the diluted mixed solution should be made up each day.

The determination is returned as the number of c.c. of the standard solution required to match the 50 c.c. of the extract.

*USE OF WOOD SPIRIT IN PLACE OF METHYL ALCOHOL.*—It will be realised that the use of pure methyl alcohol makes this test very expensive. Attempts were therefore made to see whether it were possible to use purified wood spirits. Wood spirits were found to give results which differed amongst themselves. Attempts at purification were not encouraging as, of course, a variation which meant the alteration of 1 c.c. of the standard solution is significant, and such variations occasionally occurred. It has, however, been found quite simple in laboratories, using this method regularly, to standardise each tin of purified wood spirit against pure methyl alcohol. In our laboratory four flours or so are extracted with, in the first case, pure methyl alcohol, and in the second the purified wood spirit. The necessary correction is thus found, and this is applied to all the future tests using that delivery of wood spirit (a matter of 170 determinations). It is, of course, advisable to use as good a wood spirit as possible.

*RESULTS.*—It will be realised that by the use of this method the miller can obtain a definite colour figure for his flour. He can check variations and ensure the maintenance of any special standard. In interpreting the results it is suggested that the grade figure, *i.e.* the alkaline methyl alcohol figure, should be first

considered. This indicates the brightness of the flour and its freedom from minute branny specks. Those accustomed to milling practice rapidly associate with the number, the colour of the flour, and can visualise exactly what it means in this respect. High grade patent flour will have a figure of 4.0-6.0, straight run flour 9.0-10.5, while many commercial flours of lower grade will give 11.0-12.0 and over. Then the yellowness of the flour should be considered; this is given by the petrol figure. A combination of these two will tell the miller all he wishes to know about colour.

A bleached flour will give a petrol figure of 4.0-6.0, whilst an unbleached flour is normally about 10.0. Unbleached Durum flour will give a distinctly higher figure. It must be realised that the petrol figure does not in any way differentiate high and low grade flours. This will be clearly seen later.

TABLE I.

Flour.	Petrol figure.	Methyl alcohol figure on the flour.	Methyl alcohol figure on the bread.	Ash content. Per Cent.
C.453	6.0	11.0	8.0	0.51
A.369	10.5	10.0	6.0	0.44
D.16	14.0	4.5	3.5	0.33
C.454	6.0	8.0	6.5	0.41
C.455	5.5	10.0	8.5	0.49
N.21	5.5	8.0	7.0	0.42
J.1	7.5	4.5	3.5	0.34
J.2.	8.5	8.0	7.0	0.43
A.1	6.0	11.0	8.0	0.52
A.2	7.0	7.5	6.0	0.46
M.1	9.0	9.0	8.0	0.50
E.1	4.5	8.5	6.5	0.44
C.1	6.0	11.5	8.0	0.52
C.2	6.0	8.0	6.5	0.43
A.1	9.5	8.0	6.5	0.44
M.2	8.5	11.5	9.0	0.55
C.3	5.5	9.0	7.0	0.44
C.4	6.0	12.0	9.5	0.58
M.3	8.0	11.0	9.0	0.52

Table I gives a selection of results on commercial flours. To assist comparison the ash contents of these flours are also given, as ash determinations are consistently made to check flour grade. It should be noted here that there have been many attempts to check and find a control for flour grade by the determination of analytical data. Jacobs and Rask (1920) have suggested the determination of the pentosan content, numerous investigators the counting of wheat hairs, etc., Wender (1905), and later Miller (1909), Bailey (1917), and Marion (1920) the determination of the catalase activity. It is our belief that the determination of this grade figure will give, quite simply, the best indication possible of grade. In Table I, besides the colour figures obtained with the flours, there are included the results obtained from the extraction of the crumb of the cut loaf (made from the flour). The procedure for this was exactly the same as for the flour, 20 grms. of bread crumbs (free from crust) being taken. It will be seen that the grade figures obtained from the breads correspond to these from the flours, although they are

on a slightly different plane. The petrol figures on breads were not determined, as no extraction of carotol occurred. Apparently, after baking, carotol is no longer soluble in petrol.

Table II gives the results obtained from the flour from the various rolls of a South of England mill.

TABLE II.

Flour.	Petrol figure.	Methyl alcohol figure on the flour.	Methyl alcohol figure on the bread.	Ash content. Per Cent.
A.	10.5	5.5	4.0	0.35
B.	10.5	5.0	3.5	0.30
C.	10.5	4.5	3.5	0.30
D.	11.0	6.0	5.0	0.36
E.	12.5	7.0	6.0	0.40
F.	12.5	10.0	8.0	0.53
G.	12.5	10.0	8.0	0.46
H.	12.5	12.0	10.0	0.60
J.	12.0	19.0	16.5	0.88
K.	14.5	18.5	14.0	0.71
L.	14.0	18.5	14.0	0.70
M.	14.5	21.0	17.5	0.93
Straight Run	5.0	9.0	7.0	0.40
Lower Grade	5.5	13.0	10.0	0.47
Second Patent	5.0	6.5	5.0	0.37
Top Patent	5.0	6.0	4.0	0.37
1st Break	9.5	10.0	8.5	0.53
2nd Break	12.5	11.0	9.0	0.55
3rd Break	14.5	14.0	11.0	0.66
4th Break F.	14.5	26.0	23.0	0.93
4th Break C.	14.0	25.0	21.0	0.92
Alpega	12.0	10.0	8.0	0.47
CMD	11.0	10.0	7.5	0.51
FMD	10.0	10.0	7.5	0.49

Table III gives the petrol figures of a few flours before and after bleaching by various commercial bleaching agents.

TABLE III.

## A.—NITROGEN PEROXIDE (ELECTRICAL) TREATMENT.

A patent flour—unbleached	..	..	..	..	8.0
ditto bleached	..	..	..	..	4.0
*A household flour—unbleached	..	..	..	..	12.0
ditto bleached	..	..	..	..	4.5
A lower grade flour—unbleached	..	..	..	..	8.0
ditto bleached	..	..	..	..	4.0
An all English flour—unbleached	..	..	..	..	11.0
ditto bleached	..	..	..	..	4.0

## B.—AGENE PROCESS (NITROGEN TRICHLORIDE).

A straight-run flour—unbleached	..	..	..	..	10.0
ditto bleached	..	..	..	..	4.0
A patent flour—unbleached	..	..	..	..	9.0
ditto bleached	..	..	..	..	3.5

TABLE III.—*continued.*

## C.—(NOVADELOX) BENZOYL PEROXIDE.

A patent flour—unbleached	..	..	..	..	10.0
ditto bleached ( $\frac{1}{3}$ oz. per sack)	..	..	..	..	5.0
ditto ( $\frac{1}{2}$ oz. per sack)	..	..	..	..	3.0
A lower grade flour—unbleached	..	..	..	..	15.0
ditto bleached ( $\frac{1}{3}$ oz. per sack)	..	..	..	..	11.0
“ “ ( $\frac{1}{2}$ oz. per sack)	..	..	..	..	9.0
“ “ (1 oz. per sack)	..	..	..	..	5.5

## D.—CHLORINE.

A patent flour—unbleached	..	..	..	..	8.0
ditto bleached ( $\frac{1}{2}$ oz. per sack)	..	..	..	..	6.5
“ “ (1 oz. per sack)	..	..	..	..	4.5
A lower grade flour—unbleached	..	..	..	..	9.5
ditto bleached ( $\frac{1}{2}$ oz. per sack)	..	..	..	..	6.5
“ “ (1 oz. per sack)	..	..	..	..	5.0

## NATURAL AGEING.

A patent flour—unbleached	..	..	..	..	8.5
ditto after one week's ageing	..	..	..	..	7.5
“ “ two weeks' ageing	..	..	..	..	6.5
“ “ five weeks' ageing	..	..	..	..	4.0
“ “ nine weeks' ageing	..	..	..	..	2.5
*A household flour—unbleached	..	..	..	..	10.0
ditto after one week's ageing	..	..	..	..	8.5
“ “ two weeks' ageing	..	..	..	..	6.0
“ “ three weeks' ageing	..	..	..	..	4.0
“ “ five weeks' ageing	..	..	..	..	3.0
“ “ six weeks' ageing	..	..	..	..	2.0

\* This flour was made from a blend containing a percentage of the very yellow Durum wheat.

INTERPRETATION OF RESULTS.—A general survey of Table I shows that the alcohol figures of the flours are closely correlated to the ash contents. As the alcohol figure indicates the grade of the flour, this is expected. The grade of the flour determines to a very large measure the brightness or sheen of the crumb of the loaf, so that these alcohol figures are a measure of what some millers and bakers call the “bloom” of the loaf. The petrol figure has no relation to the alcohol figure, but from Table III it can be seen that this figure gives a very good indication of the amount of bleaching which the flour has undergone. From the results in Table II it is seen that the petrol figure gives no indication of grade. For instance, the high grade flour has a similar figure to the very low grade flour.

It is interesting to examine some of the flours in Table I in the light of the information obtained by these colour figures. The figures for C.453 indicate that this flour is a fairly low grade bleached flour, whereas A.369 is probably a straight-run unbleached flour. D.16 would suggest an unbleached very high grade patent flour. J.1. and J.2 are flours from the same mill and the colour figures indicate that they are a high grade patent and possibly a straight-run, respectively, both being slightly bleached. M.1 is probably a straight-run flour.

With attention to the procedure indicated and by the use of the special colorimeter described, a high degree of accuracy can be obtained. Results are returned to the nearest 0.5 c.c. (of standard solution used). In this way duplicates by different observers usually tally exactly and never vary more than 0.5 c.c. It

is also possible to shorten the time of standing, both with the petrol and with the alkaline methyl alcohol. Good results have been obtained within three hours or less of starting the test.

It is further suggested that the form of colorimeter described may be of real assistance in other cases where comparisons of colours are required, *e.g.* water analysis and the colorimetric determination of traces of metals. A greater degree of accuracy and certainty would be obtained, and there is the additional advantage that it is independent of outside light. This, therefore, allows the test to be carried out at any time.

SUMMARY.—It has been shown that the colour of flour may be expressed by the tints given to two distinct solvents. The yellow colour of flour is extracted by petrol and its evaluation determined simply in the special form of colorimeter described. This petrol figure indicates the natural whiteness or alternatively the artificial bleach of the flour. The grade of the flour may be judged by the amount of the reddish-brown pigment present, which presumably comes from the finely powdered offal. This can be estimated in the same colorimeter after extraction, in the manner described, by alkaline methyl alcohol. A consideration of the two estimation figures thus obtained gives full information as to the colour of the flour. The method has the advantage that personal judgment is largely eliminated, and also that a numerical expression for colour is obtained.

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#### DISCUSSION.

The CHAIRMAN (Mr. John White) emphasised the need for a scientific apparatus for testing the colour of flour. He remarked that in the old days samples of flour used to be put in dark blue boxes for the purpose of showing up their whiteness.

Dr. MONIER-WILLIAMS asked whether the methyl alcohol figure was absolutely unaffected by bleaching.

Mr. E. HINKS asked whether the other conditions (apart from the use of tap water and the given solution) used by the various experimenters were identical and where the conditions were precisely described. He mentioned that it had

commonly been stated that bleaching was resorted to in order to disguise particles of bran, but the authors' work seemed to show that bleaching did not effect this.

Mr. C. A. MITCHELL wondered whether the instrument could be combined with the Lovibond tintometer, as in the case of Osborne's tintometer microscope, so that a reading in reds, yellows, and blues could be obtained and recorded.

Mr. HERD replied that each analyst had made a report on the quality of the flours submitted, and these agreed very well. The gluten was dried in a water oven, at 98.5° C. for twenty-four hours. An extra twenty-four hours' drying gave only a slightly different result. With respect to the colour paper; bleaching did not affect the methyl alcohol figure. The adjustment of the depth of the solution did not give satisfactory results: a good depth of solution was required. Combination with the Lovibond tintometer had not been attempted, as the present instrument gave the figures (representing brightness and yellowness) the millers required; they were not concerned with differentiation into component colours.

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## Cacao Butter Substitutes and Their Detection.

BY A. W. KNAPP, J. E. MOSS AND A. MELLEY.

(Read at the Meeting, March 2, 1927.)

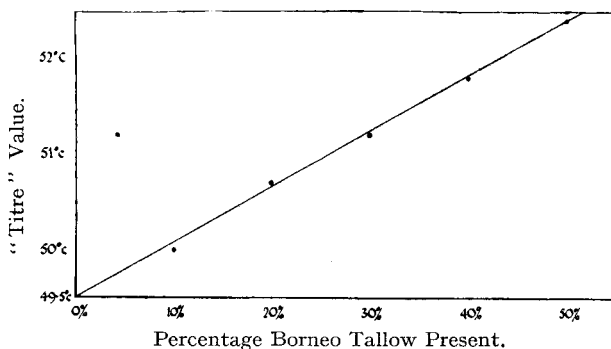
THE cacao butter substitutes that are advertised in the trade papers are not usually sold under their true name, but under a trade name. One finds, however, that reputable sellers always endeavour to supply under these trade names the same fat or mixture of fats. As a result of the examination of a large number of substitutes we arrive at the conclusion that, of the many possible substitutes, only (a) coconut or palm kernel stearin, and (b) the so-called illipé butters, are of commercial importance.

The presence of as little as 5 per cent. of coconut or palm kernel stearine can be readily detected. It does not appear to be generally known that with pure cacao butters which are not rancid neither the Reichert-Meissl nor Polenske value rises above 0.3.

A number of fats which are used as substitutes for cacao butter are known commercially as *illipé butter*. (They must not be confused with the true illipé fats obtained from *Bassia longifolia*.) Of these, by far the most important, and the one which most nearly resembles cacao butter, is Borneo tallow, prepared from Pontianak or Sarawak nuts (*Shorea stenoptera* and kindred species). A few manufacturers use the "Siak" nut, which is a totally different species (*Palaquium oblongifolium*, which belongs to the same family as *Bassia*). This is distinguished by a high melting point (40° C.) combined with a high iodine value (51 per cent.). Some authorities (e.g. *Bulletin Imperial Institute*, 1915, p. 337, and Lewkowitsch, 1914, Vol. 2, p. 601) state that this fat is softer than Borneo tallow. This is incorrect. Sometimes small quantities of other fats are mixed with Borneo tallow the most commonly found being mowrah seed oil and shea butter. Both of these have high iodine values and high Zeiss refractometer figures, which make their presence easy of detection.

In France the use of Borneo tallow and fats other than cacao butter in plain chocolate is illegal. The Chambre Syndicale of the chocolate manufacturers of France offered, in 1923, a prize of 20,000 francs for a method of detecting substitutes. Up to date they have not been able to award the prize, as they do not consider any of the processes offered are sufficiently satisfactory.

THE "TITRE" OF THE FATTY ACIDS.—The most useful single figure we at present possess is the "titre" of the fatty acids. This figure for cacao butter shows very little variation, the range being from 49° C. to 50° C., whilst the mean value for Borneo tallow is 54.6° C. From our observations, it is safe to assume that any



sample of cacao butter is adulterated if it gives a "titre" over 50° C. Provided certain other oils (*e.g.* coconut) are not present, the amount may be roughly estimated from the curve shown. As the method of obtaining the fatty acids affects their composition, this is described below:—

About 60 grms. of the fat are placed in a porcelain cup and boiled with alcoholic potassium hydroxide solution (20 grms. in 60 c.c. of alcohol) until the fat is saponified and the smell of alcohol is only faint. The mixture is transferred to a large porcelain dish, about 600 c.c. of water added, and the whole boiled down to half its bulk. The residue is now put into a large beaker, and sulphuric acid 50 per cent. v.v added until it is in excess; that is, until the mass breaks up and floats. The beaker is then placed on the water bath and left until the whole contents become quite clear, the top being covered with a clock glass. When the mixture has remained still for a few moments on the top of a water oven, the lower liquid is siphoned off, the fatty acids washed with a 5 per cent. (volume for volume) sulphuric acid solution by shaking in a separator, allowed to separate and the sulphuric acid layer run off. The fatty acids are then transferred to a beaker and allowed to cool, and their "titre" is then determined by Dalican's method.

SOLUBILITY TESTS.—Of the various tests which have been suggested for detecting "green butters," that is, cacao butter substitutes such as Borneo tallow, or fats artificially coloured to imitate Borneo tallow, the Halphen test (ANALYST, 1908, 33, 468) has received some attention. In Revis and Bolton's transcription of the test (ANALYST, 1913, 38, 201) the amount of fat and carbon tetrachloride mixture which is taken is incorrectly quoted as 2 c.c.; it should be 1 c.c.

The test was published in 1908, and may have been a good test for the "green butters" then on the market, but, with the refined Borneo tallow which is produced to-day, it fails. In those cases where shea butter or *Bassia* fats are present it gives fair results, which might possibly be used to support other evidence.

Revis and Bolton's modification of this test (ANALYST, 1913, 38, 201) is a test for *cacao butter* in the presence of "green butters," or for differentiating between cacao butter and "green butters." It is questionable whether the specification of the petroleum spirit, which is that part distilled below 40° C., is sufficiently complete. We find the test is of somewhat narrow application; most fats, however, give turbidities, and it is distinctive of refined Borneo tallow that it gives perfectly clear solutions. The following points should be noted:—(1) Some solvent-extracted cacao butters act in the same way as Borneo tallow—so do some coconut stearines. (2) The presence of shea butter, even though refined and filtered, interferes with the test, giving a yellow, resinous body, turning black on standing. (3) Phulwara fat (from *Bassia butyracea*) gives a very similar canary yellow precipitate to cacao butter.

TATE AND POOLEY'S METHOD.—Tate and Pooley's method of estimating Borneo tallow in cacao butter (ANALYST, 1921, 46, 229) is useful if applied with discretion. Preferably the analyst should determine his own average constants. If other substitutes are present besides Borneo tallow, it is better to examine critically all the figures, rather than to depend on this calculation. For example, the low "titre" in mixture (2) below suggests the probable presence of up to 10 per cent. of coconut stearine, a percentage which could be accurately determined by the Reichert and Polenske value, etc., and its interference with the other figures appreciated. The following figures may be of interest in this relation:—

	Cacao butter from Grade I Accra cacao beans.	SUBSTITUTES.			MIXTURES.		
		English refined Borneo tallow.	Coconut stearine substitute.	Refined shea butter.	1 Cacao butter with 15 per cent. Borneo tallow.	2 Cacao butter with 10 per cent. Borneo tallow and 10 per cent. Coconut stearine	3 Cacao butter with 10 per cent. Borneo tallow and 10 per cent. shea butter.
Specific gravity at 60° C./15° C.	0.8831	0.8820	0.8936	0.8888	0.8830	0.8838	0.8816
Specific gravity at 99.9° C./15° C.	0.8562	0.8557	0.8668	0.8644	0.8559	0.8567	0.8580
Viscosity at 60° C. (secs.)	102	114	66	126	103	101	103.5
Melting point (°C.)	32.6	36.2	32.4	33.4	33.2	32.6	33.6
Iodine value	38.4	34.8	4.02	51.3	37.98	33.43	37.97
"Titre" value of fatty acids (°C.)	49.0	54.1	27.7	50.2	49.4	47.2	50.2
Tate and Pooley's factor	3208	4839	1141	3164	3362	3521	3477
Calculated percent- age of Borneo tallow from Tate and Pooley's fac- tors	—	—	—	—	19.9	33.3	29.8



According to Tate and Pooley, the average factor for cacao butter is 3150, and for Borneo tallow 4403.

In the above the "titre" of the fatty acids is given instead of the melting point, because, in our experience, different observers show closer agreement for the "titre." It will be noted that, whilst the individual figures for shea butter are very different from those of cacao butter, the factor is within the range for cacao butters, and, therefore, shea butter would not be detected. On the other hand, in the case of mixture (1), owing to the low "titre" of the cacao butter used, no single figure would suggest adulteration, whereas Tate and Pooley's factor clearly indicates it.

**PERMANENCE OF THE GREEN COLOUR.**—The green colour of Borneo tallow is striking and characteristic. The yellow colour of cacao butter is readily bleached by daylight, but the green colour of Borneo tallow is comparatively resistant to ultra-violet light. It was thought that a method of detection and approximate estimation might be founded on this fact. The method finally adopted was as follows:—

Thirty grms. of the fat were placed in a Petri dish, 15 cm. in diameter, and exposed for 6 hours 6.5 inches below a quartz mercury vapour lamp, the Uroxameter value\* of which was 28.0 per cent. The period of exposure should vary inversely with the strength of an ultra-violet lamp as indicated by the Uroxameter value. After exposure the fat was filtered into a 5/8 in. test tube, and the intensity of green colour compared with a set of standard exposed fats obtained from a series of fats with 0, 5, 10, 20, 30, 40, 50, and 75 per cent. of Borneo tallow in cacao butter. The test tubes are placed on a white tile, and viewed vertically through the 5½ inches of fat.

A series of butters was supplied by Dr. H. W. Bywaters, who did not disclose their composition, and on examination according to the above process, the following results were obtained:—

BORNEO TALLOW IN CACAO BUTTER MIXTURES.

Reference number of fat.	Percentage of Borneo tallow found by above process.	Actual percentage of Borneo tallow as per key	Percentage of Borneo, tallow found by visual examination of original mixtures.
1.	22	15	5
2.	12	9	0
3.	60	44	30
4.	45	34	25

In order to determine whether the bleaching of the cacao butter in the mixtures allowed of a more accurate colorimetric comparison, the tints of the unexposed butters were compared with a series of standards comprising unexposed mixtures of 0 to 75 per cent. of Borneo tallow in cacao butter. The results are given in the last column above. It will be observed that it is with the determination of quantities of Borneo tallow less than 20 per cent. that the ultra-violet light treatment gives a considerably more accurate result than obtained by comparison of unexposed mixtures.

\* For method of determining this see *J. Soc. Chem. Ind.*, 1925, **44**, 453T.

Whilst Borneo tallow cannot be easily bleached, a true Borneo tallow has been offered for sale from which the colour has been practically removed. It is white, with only a suspicion of green. Obviously the method would fail with this fat.

An attempt was made to extend the test to the detection of Borneo tallow in chocolate. The results were unsatisfactory, as the green colour is not quantitatively extracted by petroleum spirit.

BYWATERS' PROCESS:—The process described by Dr. Bywaters and his collaborators (ANALYST, 1927, 324) depends partly on the peculiarly large amount of super-cooling which cacao butter can undergo, and partly on the presence in Borneo tallow of certain high-melting glycerides or unsaponifiable bodies. If these are only a small fraction of the Borneo tallow, there is always the possibility that different manufacturers may leave different amounts of them in their products, and thus vitiate the method.

The process is valuable, in that it provides an entirely new figure. In our hands with known mixtures it has given results which were often remarkably accurate, but also results which were quite wide of the mark.

The following table gives some figures obtained by Mr. A. Churchman:

Borneo Tallow present. Per Cent.	Turbidity point. °C. °C. °C.	Borneo tallow found. Per Cent.
4	21·7, 21·7	2·7
6	22·1, 22·1	7·4
8	22·1, 22·0	7·0
(a) 10	22·2, 22·7	8·5 to 13·8
(b) 10	21·4, 21·5, 21·5	1·0
(a) 20	22·5, 22·7, 22·6	12·8
(b) 20	22·7, 22·3	9·6 to 13·9
30	23·8, 24·0	26·6
40	24·7, 24·7	35·1
45	25·4, 25·3	42·0
(a) 50	26·1, 26·0	49·5
(b) 50	25·8, 25·9, 25·8	46·8

(a) English refined.

(b) French refined.

It appears to be almost impossible to define the conditions with sufficient accuracy to ensure concordant results. After all, the temperature to which a liquid can be super-cooled is dependent on so many factors. For example, it depends on the previous history of the liquid fat, and in particular whether it contains any solid nuclei. We would suggest that the fat at the beginning of the experiment be raised to an agreed temperature sufficiently high to ensure that the whole of the constituents are in a completely liquid condition. Ideally the fat should begin to become turbid round the bulb of the thermometer, but, in practice, turbidity may inconveniently appear in other parts of the tube. It seems probable that where the fat has first to be extracted from chocolate the solvent used may have some effect on the properties of the fat obtained.

In conclusion, we wish to thank Messrs. Cadbury Brothers, Ltd., for their permission to publish the above.

## The Effect of Common Salt on Lime Water Used for Egg Preserving.

By JAMES MILLER, F.I.C.

(Read at the Meeting of the Northern Section, February 26, 1927.)

THE efficiency of lime water for preserving eggs depends on the liquid retaining its lime strength.

On standing in air, lime water becomes coated with a film of calcium carbonate which increases in thickness and protects the lime water underneath from attack by the carbon dioxide in the air.

In the trade the skin so formed is spoken of as "ice," and the description is felt to be appropriate when one sees a large tank of lime water after it has stood for a week or two. Thus protected, the lime strength decreases very slowly.

Clean fresh eggs immersed in lime water will keep for twelve months, provided the "ice" remains unbroken, and the solution retains its lime strength. If, however, eggs are cracked when being put down, or the "ice" is repeatedly broken, the lime content of the liquid decreases, and finally becomes *nil*, thus rendering the solution useless for preserving purposes.

It seems to be a common practice to add common salt to lime water for egg preserving, one object being to increase the specific gravity of the liquid and thus minimise breakage in the lower layers of eggs. From results obtained on a large scale, it was thought desirable to investigate the effect, if any, of common salt on lime water.

Lime water was prepared with water alone and with water containing common salt equivalent to 1, 10, 100, and 500 lbs. per 1000 gallons, respectively. Quantities of 500 c.c. of each were allowed to stand in beakers (3¼ in. diameter), covered loosely, and the lime strength of the clear liquid was determined at intervals of 1 month.

The following results were obtained:—

Common salt, lbs. per 1000 galls.	LIME WATER.						
	Lime, (CaO) lbs. per 1000 galls.						
	At start.	1 month.	2 months.	3 months.	4 months.	5 months.	6 months.
None	13.1	9.9	9.3	9.0	8.1	7.2	6.2
1	13.2	10.4	9.9	9.5	8.3	7.2	6.0
10	13.7	10.5	9.6	6.6	2.7	0.15	Nil
100	15.6	8.7	4.5	Nil	Nil	Nil	Nil
500	17.6	10.1	0.3	Nil	Nil	Nil	Nil

After standing for one month all were covered by a good skin, but with 100 and 500 lbs. common salt, respectively, the skin was "sweating."

After standing for six months, there was a good skin on the solution containing no salt, and on the one containing the equivalent of 1 lb. of salt, but on the 10 lbs. salt solution the skin was broken and "sweating."

LIME WATER WITH EXCESS OF LIME.—Quantities of 500 c.c., as in the preceding experiments, were prepared containing 2.6 grms. of calcium oxide

(four times the solubility of lime in water) and common salt equivalent to 1, 10, 100, and 500 lbs. per 1000 gallons, respectively. The mixture was well stirred and allowed to settle overnight. The lime strength of the clear liquid was determined and repeated at intervals of 1 month.

Common Salt. lbs. per 1000 galls.	LIME WATER WITH EXCESS OF LIME.							
	Lime (CaO) lbs. per 1000 galls.							
	At start.	1 month.	2 months.	3 months.	4 months.	5 months.	6 months.	Stirred.
None.	12.9	12.2	12.6	12.8	13.2	12.9	13.0	12.5
1	12.9	12.3	12.6	12.6	13.1	13.0	12.9	12.6
10	13.4	11.7	12.1	12.3	12.7	11.4	9.9	12.3
100	15.6	7.4	5.2	4.8	3.7	0.15	0.05	0.05
500	17.9	6.0	4.5	0.15	Nil	Nil	Nil	Nil

Good skins formed on all the solutions, but after one month the pickles containing 100 and 500 lbs. salt shewed "sweating," and the solutions were cloudy for about two inches down.

After six months, there was a good skin on the solution containing no salt and on the one containing 1 lb. of salt, and 10 lbs. of salt respectively. The skins on the solutions with 100 and 500 lbs. salt were broken and "sweating."

At the end of six months, all the pickles were stirred, allowed to settle, and the lime strength again taken. It will be seen that in the case of those containing 100 and 500 lbs. salt all the settled lime had been carbonated.

From the first table it appears that lime water containing 100 lbs. of common salt per 1000 gallons does not retain its lime strength, and the second table shows that even in pickle containing excess of lime the total lime is completely carbonated in the presence of 100 lbs. or more of common salt per 1000 gallons.

The method of preparing lime water, given in "The Storage of Eggs," Department of Scientific and Industrial Research, Special Report No. 26, and recommended by the Board of Agriculture and Fisheries Leaflet No. 83, is as follows:

"*Lime Water.* Four parts of finely slaked lime are mixed with twenty parts of cold water and the whole well mixed for several days to ensure saturation. One part of salt is then added and the clear solution decanted and poured over the eggs which should be placed in suitable wooden, cement or galvanised iron containers."

From the results obtained the following criticisms of the above method may be offered:—

The solubility of lime in water is about 1 in 750; therefore, the above amount of lime seems excessive. Tap water mixed with four times the amount of burnt lime necessary to saturate it was stirred for five minutes and allowed to settle; the liquid contained 12.6 lbs. of calcium oxide per 1000 gallons, which is practically a saturated solution; therefore, mixing for several days to ensure saturation is quite unnecessary.

One part of salt to twenty parts water is equivalent to 500 lbs. per 1000 gallons; from the tables given it will be seen that this amount is not only unnecessary but detrimental.

## The Natural Occurrence of Boron Compounds in Cacao and Cacao Products.

By A. SCOTT DODD, B.Sc., F.I.C., F.R.S.E.

NATURAL OCCURRENCE OF BORIC ACID.—The existence of boron compounds as natural constituents of various articles of food has been pointed out by numerous observers from time to time. In most cases the quantity found was very small, and was until recently considered to be of little consequence. The introduction of the Public Health (Preservative) Regulations, 1926, has, however, put a different complexion on the matter, and made the question of the natural occurrence of certain preservative compounds in food an exceedingly important one. These regulations absolutely prohibit the use of boron compounds for preserving articles of food, but make no provision for the existence of those which may be present through unavoidable causes.

Mr. A. Chaston Chapman (*ANALYST*, 1926, **51**, 215) sounds a note of warning regarding the natural occurrence of formaldehyde in boiled sugar, sweets, caramel and other articles prepared by the heating of carbohydrates. A similar warning is given by Tankard and Bagnol (*ANALYST*, 1926, **51**, 565) relating to formaldehyde in fish. Benzoic acid is also known to occur as a normal constituent of certain fruits, such as cranberry, bilberry, etc., and is therefore liable to be found in some jams and tarts.

Boron compounds are very widely diffused in nature and have for long been known to exist in sea water (Nöllner, *J. prakt. Chem.*, 1867, **102**, 463; *Compt. rend.*, 1881, **93**, 224; 1882, **94**, 1352). Hence its occurrence in Irish moss, seaweed (*Fucus*), and agar agar, as pointed out by Chapman and Linden (*ANALYST*, 1926, **51**, 564). These investigators found boron compounds to exist in seaweeds in quite appreciable quantities, namely, equivalent to 0.097 per cent. and 0.076 per cent., boric acid in Irish moss and 0.04 per cent. boric acid in *Fucus*, while in agar agar it appears to be even more abundant, varying from 0.07 per cent. to 0.16 per cent. expressed as boric acid.

It has also been shown that boron compounds may be found in certain mineral waters (Gooch and Whitfield, *Bull. U.S. Geol. Survey*, 1888, No. 47; Fonzes-Diacon and Farbe, *Compt. rend.*, 1914, **158**, 1541).

The wide diffusion of boron compounds throughout the vegetable kingdom is shown by the prolific literary publications on the subject which have appeared in the scientific journals of Great Britain, America, France, Germany, and Italy, etc. J. Brand (*Z. gesammt. Brauw.*, 1892, **15**, 427), shows that beer may contain boric acid, which has been introduced through boron compounds existing as natural constituents of hops. H. Jay and Dupasquier (*Comptes Rend.*, 1895, 260–262), investigated certain animal and vegetable products and proved that wines contained boric acid, which had not been added either accidentally or intentionally. In the *Z. Untersuch. Nahr. Genussm.* (1902, **5**, 1044) reference is

made to boric acid existing naturally in the juice derived from cherries, gooseberries, oranges, and lemons. A. H. Allen and A. R. Tankard (*ANALYST*, 1904, **29**, 301) give a large number of English references which show the natural occurrence of boron compounds in grapes (and therefore wine), apples and pears (and consequently in cider and perry), radishes, lettuce and water-melons. They showed that the quantity of boron compounds found in their own investigations on apples, pears, quinces, pomegranates, and grapes was very small, namely, 0.004 per cent. to 0.016 per cent. expressed as boric acid, and in the case of cider that the quantity was merely 0.004 per cent. to 0.0017 per cent., expressed as boric acid.

A source of introduction of boron compounds into manufactured articles appears to be through the medium of common salt. R. Hefelmann (*Z. öffentl. Chem.*, 1905, **11**, 231) states that boric acid is undoubtedly present in common salt mined in Italy and certain districts of Germany, but that the quantity is extremely small, varying from 0.0006 per cent. to 0.003 per cent. Naturally if this salt were used for flavouring meats or for salting butter or margarine, the amount of boric acid thus introduced would be too small to be detected. V. Villavecchia and I. Barboni (*Ann. Lab. Chim. cent. delle Gabelle*, 1912, **6**, 27-68) point out, however, that most of the samples of Italian salt they examined contained appreciable amounts of boric acid, reaching a maximum quantity of 3.25 per cent. in Salsomaggiore salt. These investigators found that various samples of Italian charcuterie contained from 0.004 per cent. to 0.020 per cent. of boric acid, and suggest that a limit of 0.02 per cent. should be fixed as the maximum permissible limit for boric acid unintentionally introduced with the salt into flesh products.

An investigation by G. Bertrand and H. Agulhon (*Compt. rend.*, 1914, **158**, 201), embracing a wide range of articles, indicates the existence of boron compounds as natural constituents of apricots, cherries, figs, strawberries, peaches, pears, apples, raisins, carrots, haricot-beans, onions, peas, potatoes, tomatoes, wheat, milk and eggs. The quantity of boric acid found in both milk and eggs is extremely minute, and amounts to merely 0.00011 per cent. and 0.000014 per cent., respectively. Among the fruits and vegetables examined the boric acid content was found to vary from 0.00056 per cent. in wheat to 0.01126 per cent. in apricots, cherries, strawberries, peaches, carrots, and peas. These last results represent the quantity of boric acid calculated to the dry substance, and it is noteworthy that these authors made all the determinations of boric acid by a method devised by themselves and depending upon the coloration of strips of turmeric paper immersed partly in the boric acid solution (G. Bertrand and H. Agulhon, *Comptes rend.*, 1913, **157**, 1433).

From these results, as indicated by the publications mentioned, it would appear that boron compounds are liable to be detected in almost all classes of food and drink. The main point, however, which is of importance to a Public Analyst, now that boron compounds may no longer be added for preservative purposes, is that of making a distinction between boron compounds which have

been knowingly added, and those which occur as natural normal constituents of the raw materials from which the article of food has been prepared. Those Public Analysts who are called upon to advise their Local Authorities regarding the institution of proceedings under the Sale of Food and Drugs Acts are now confronted with the problems of deciding (1) whether boric acid is present as a natural constituent of the article; and (2) whether the amount of boric acid found is in excess of that likely to occur as a natural constituent of the ingredients.

It is quite evident that in most foods the quantity of boron compounds likely to be derived from natural sources will be practically negligible. In many others, such as dried fruits, raisins, currants, etc., and articles manufactured therefrom boron compounds may be present in quite appreciable amounts. Much anxiety and disquietude has been caused among wine manufacturers and importers by the discovery of appreciable quantities of boric acid in sherry and various other wines and vine products. The Public Health (Preservative) Regulations, 1925, make no allowance for the presence of boron compounds in food through natural causes, and, in the absence of any authoritative statement from the Ministry or Board of Health, many manufacturers are at a loss to know whether they may safely purchase certain articles known to contain small quantities of boron compounds, without risking their reputations by coming into conflict with Local Authorities. The author, therefore, is entirely in agreement with Mr. A. Chaston Chapman (*ANALYST*, 1927, 217) that "caution must be observed in ascribing the presence of traces of boron to the use of boric preservative." The problem of differentiating between boron compounds which have been added as preservatives, and those which occur naturally, will in some cases be no easy matter, and unless the Ministry of Health supplements the existing regulations by fixing limits for preservatives, beyond which they will be regarded as "added," much confusion and injustice may take place.

In absence of any authoritative statement to aid Public Analysts in deciding when a preservative is sufficient in quantity to constitute adulteration, there is certain to be great diversity of opinion on this subject. It is, therefore, of the greatest importance to Public Analysts and all others concerned with the administration of the Sale of Food and Drugs Acts that steps should be taken by the Ministry of Health without delay to prevent the court fights over natural and added preservatives, being on a par with the existing ones relating to abnormal or adulterated milk.

**BORON IN COCOA AND CHOCOLATE.**—As an outcome of the discovery of boron compounds in certain chocolate preparations the present investigation was undertaken, and the results which are shown below in tabulated form prove definitely that boron compounds not only exist as natural constituents of cacao beans, but that the amount present is quite appreciable. The existence of boron compounds as a natural constituent of the cacao tree and consequently in articles of food, such as cocoa and chocolate, prepared therefrom does not appear to be known generally, and so far as the author has been able to ascertain is not referred to specifically in any previous publication.

Cocoa and chocolate enter into the composition of a large number of articles of food so the discovery therein of boron compounds as natural ingredients may be of considerable importance as well as interest. It is interesting to note that the quantities found in cacao beans are very similar to those found in Irish moss, seaweeds and agar agar by Chapman and Linden (*loc. cit.*).

Variety.	CACAO BEANS.					
	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Trinidad	0.0403	6.20	3.24	96.55	3.45	0.043
"	0.0465	5.48	2.60	97.15	2.85	0.049
"	0.0713	6.20	3.14	96.65	3.35	0.076
"	0.0589	4.70	3.20	96.64	3.36	0.062
"	0.0558	4.20	3.32	96.53	3.47	0.058
West African	0.0536	5.94	2.70	97.13	2.87	0.057
" "	0.0837	5.88	3.70	96.07	3.93	0.089
Nigerian	0.0514	4.90	3.60	96.21	3.79	0.054
"	0.0543	6.84	4.06	95.65	4.35	0.058
Jamaican	0.0527	4.88	3.32	96.51	3.49	0.055
"	0.0527	7.20	3.46	96.27	3.73	0.057
Arriba or Guayaquil	0.0620	4.50	3.66	96.17	3.83	0.065
" " "	0.0558	6.78	3.60	96.25	3.75	0.060
" " "	0.0682	2.80	4.08	95.80	4.20	0.070
Ceylon	0.0432	4.10	3.32	96.54	3.40	0.045
"	0.0527	4.60	3.12	96.73	3.37	0.055
Grenada	0.0698	5.04	3.08	96.76	3.24	0.073
Samoa	0.0372	7.40	4.70	94.92	5.08	0.040
Para	0.0419	6.14	3.26	96.53	3.47	0.045
Puerto Cabello	0.0217	6.68	8.12	91.30	8.70	0.023
Accra	0.0496	4.40	3.34	96.51	3.49	0.052
Caracas	0.0589	4.40	3.44	96.40	3.60	0.062

As will be observed from the following results, the quantity of boron compounds in cocoa is very similar to that found in cacao beans, but, as one would naturally expect, the quantity present in chocolate is very much less.

Variety.	ACTUAL.					
	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Cocoa 1	0.0678	4.34	7.04	92.65	7.35	0.071
Cocoa 2	0.0465	4.00	7.40	92.29	7.71	0.048
Cocoa 3	0.0837	6.34	7.26	92.25	7.75	0.089
Chocolate 1	0.0093	0.40	0.66	99.34	0.66	0.010
Chocolate 2	0.0099	0.48	0.64	99.36	0.64	0.010
Chocolate 3	0.0186	0.34	0.96	99.04	0.96	0.019

Every sample of cacao beans and cocoa which was examined qualitatively for boron compounds showed positive results by the usual turmeric paper tests. In order, therefore, to prove conclusively that these compounds really existed naturally in cacao and had not been introduced by enterprising planters to aid the keeping qualities of the cacao beans, two unopened cacao pods were obtained from Trinidad, through the kindness of Mr. A. W. Knapp, Chief Chemist to Messrs. Cadbury Bros., Bournville. These pods were quite intact when received, were



carefully opened, and the beans and other portions were separated and analysed individually. These results are shown below, and prove conclusively that boric acid does exist as a natural normal constituent of the cacao tree.

Trinidad Cacao Pods.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
(1) Epidermis	0.0124	88.20	0.60	94.92	5.08	0.105
Pulp and juice	0.0099	94.80	0.60	88.46	11.54	0.190
Beans	0.0192	65.94	0.60	98.23	1.77	0.056
(2) Epidermis	0.0192	84.88	1.00	93.39	6.61	0.127
Beans	0.0651	65.80	1.44	95.79	4.21	0.190

BORON IN COFFEE BEANS.—E. Bertarelli (*Z. Untersuch. Nahr. Genussm.*, 1900, 3, 681) calls attention to the adulteration of roasted coffee beans by the practice of pouring over them a boiling aqueous solution of borax. The practice is evidently with a view to increasing the percentage of moisture in the beans, rendering them glossy in appearance and leaving their original hardness unimpaired. The author recommends that borax should be looked for where more than 4 per cent. of water is found. Genuine roasted coffee does not usually contain more than about 3 per cent. of water, but the author has found upwards of 10 per cent. in roasted beans which have been treated in the way described.

The quantity of borax present in coffee beans adulterated in this manner will undoubtedly be so great as to leave no doubt in the mind of the Public Analyst, who detects it, as to borax having actually been added. The author has examined a large number of samples of coffee for boron compounds, and it is interesting to note that these are actually present in the coffee beans as natural constituents (*cf.* Partridge, *ANALYST*, 1927, 401). The quantity present, as is shown by the few examples given below, is very small and would be quite insignificant in comparison to that existing in coffee beans which have been subjected to the above treatment.

Article.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Coffee 1	0.0102	2.56	3.60	96.21	3.79	0.010
Coffee 2	0.0108	2.68	3.80	96.09	3.91	0.011
Coffee (unroasted)	0.0093	3.68	3.90	95.91	4.09	0.010

Coffee, however, apart from its use in the preparation of the usual beverage does not enter very largely into the composition of food. The fact, therefore, of boron compounds forming part of its natural constituents, though perhaps interesting, is of little practical significance compared with the similar discovery in respect of cacao and cacao products.

METHOD OF ANALYSIS.—In the various investigations cited the methods of determining the boric acid appear to be somewhat varied. R. T. Thomson's method, although somewhat laborious, is generally accepted as affording accurate

results. It, however, has been modified on several occasions, and in view of some difficulties experienced in its use, the writer now ventures to suggest and recommend still another modification which he has found to be satisfactory both as regards practical manipulation and results.

The method of quantitative determination of boric acid used was essentially that described in *THE ANALYST*, 1923, 48, 416, from which it differed mainly in choice of indicators, and minor practical details.

Twenty grms. of the sample, ground fairly small, were dried for two hours in a steam oven, and then washed with successive portions of dry ether by stirring in a glass and filtering through a Swedish filter paper. After the filter paper and contents had been washed free from fat the extracted sample and the ash from the filter paper were placed in a platinum basin. The ethereal extract was washed with 5 c.c. of *N* sodium hydroxide solution and then with 5 to 6 c.c. of water, the washings being added to the contents of the platinum basin. Another 5 c.c. of *N* sodium hydroxide solution was stirred into the contents of the platinum basin, and the whole evaporated on a steam bath and then heated and thoroughly charred over an Argand burner. The charred residue was, after cooling, warmed with about 10 c.c. of water, filtered into a small beaker, and washed with about 5 c.c. of water. The filter paper and charred contents were returned to the platinum basin, dried and ignited to a white ash at a dull red heat.

The contents of the small beaker were transferred to the platinum basin. This was covered with a glass plate and dilute hydrochloric acid run in with a pipette until the contents were slightly but distinctly acid. The platinum basin was placed on the steam bath, and, after the effervescence due to the escape of carbonic acid had ceased, the glass plate was washed into the basin, and the contents evaporated to about half their bulk, and then filtered into a 100 c.c. flask, the filter paper being well washed with small quantities of boiling water, and, for convenience of working, the 100 c.c. flask left not more than three parts full. Three c.c. of 10 per cent. calcium chloride solution and 5 drops of phenolphthalein solution were added, and then *N* sodium hydroxide solution with constant shaking, drop by drop, until the contents of the flask were faintly but distinctly pink. The liquid was made up to the 100 c.c. mark with water, shaken thoroughly and filtered.

Fifty c.c. of the filtrate were placed in a 200 c.c. beaker flask, 5 drops of *N* sulphuric acid in excess of that required to discharge the pink colour of the phenolphthalein added, and after the flask had been covered with a watch glass, the contents were boiled for 10 minutes to expel the carbonic acid, cooled quickly, 1 drop of Sofnol Indicator No. 1 added, and 0.1 *N* sodium hydroxide solution run in until the neutral point was reached. About 0.5 gm. of mannitol was then added, together with 10 drops of phenolphthalein solution, and the whole titrated to a pink colour with 0.1 *N* sodium hydroxide solution. Another portion of mannitol was added, but, if the colour was not discharged, the titration was considered to be complete.

In order to ascertain if the phosphates had been completely precipitated, the contents of the beaker flask were tested for calcium salts by heating with acetic acid and ammonium oxalate solution. A positive reaction indicated that sufficient calcium chloride had been added to precipitate all the phosphate.

The number of c.c. shown in the titration, multiplied by 0.062, gives the percentage of boric acid ( $H_3BO_3$ ).

The use of methyl orange indicator, though theoretically sound, and usually mentioned in text books and elsewhere in detailing Thomson's process, is far from satisfactory from a practical point of view. The end point, when neutralising the solution with 0.1 *N* sodium hydroxide, is not sharp, and in many cases is too indefinite to ensure accuracy. Paranitrophenol is certainly much better, but there is some disadvantage in the fact, that in the final titration the beautiful colour reaction of the phenolphthalein is distinctly marred by the dirty yellowish brown due to the interaction between the alkali and the paranitrophenol.

Methyl red has been found to give quite good results, but, of all the indicators which were tried, the greatest satisfaction was obtained by the use of an alcoholic solution of Sofnol Indicator No. 1, manufactured by Sofnol Ltd., Greenwich. This indicator has a  $P_H$  value of 6.5, is unaffected by dilute solutions of boric acid and gives a very sharp end point, the change from pink to yellow being effected by less than a drop of 0.1 *N* sodium hydroxide.

**QUALITATIVE TEST FOR BORIC ACID.**—In dealing with substances which contain only small percentages of boron compounds it is essential to take special precautions to ensure satisfactory and conclusive reactions. Owing to the volatility of boric acid in oily substances, even when ignited in presence of an excess of alkali, it is advisable, when dealing with substances which contain much oil, to remove the bulk of oil first. From 5 to 6 grms. of the original sample were mixed with 1 c.c. of *N* sodium hydroxide solution and gently ignited and ashed at a dull red heat. The ash was heated on a steam bath with 10 to 15 drops of water and a sufficient number of drops of concentrated hydrochloric acid to render the solution slightly, but distinctly, acid. A strip of freshly prepared sensitive turmeric paper was dipped in repeatedly (alternately drying on side of the basin and dipping in) until the bulk of the boric acid present was transferred to the test paper. This, when dry, gave a rose pink colour, which changed to green when touched with dilute sodium hydroxide solution.

**PREPARATION OF SENSITIVE TURMERIC PAPER.**—This test paper was prepared by dipping strips of fairly thick blotting paper into a solution containing 2 grms. of turmeric, 2 grms. of tartaric acid, and 100 c.c. of 80 per cent. alcohol. The paper, when evenly stained, was hung up to dry in the dark, and was then cut into narrow strips. It is essential for this test that the paper be freshly prepared or not more than about a month old. (Cribb and Arnaud, *ANALYST*, 1906, 31, 148.)

The following is a brief summary of the main conclusions arrived at by this investigation:—(1) The introduction of the Public Health (Preservative) Regulations, 1925, has rendered a fuller knowledge of the natural occurrence of certain preservative compounds in food imperative.

(2) Boron compounds exist as normal constituents of cacao and cacao products in quite appreciable amounts. The quantity in chocolate is about 0.010 per cent., expressed as boric acid ( $H_3BO_3$ ), and that in commercial samples of cacao beans and cocoa varies from 0.0217 per cent. to 0.0837 per cent., expressed as boric acid.

(3) Boron compounds also exist as natural constituents of coffee beans, but the quantity is very small, amounting to about 0.010 per cent. expressed as boric acid.

(4) Greater accuracy and facility of manipulation is ensured by the use of Sofnol Indicator No. 1 in place of Methyl Orange Indicator in R. T. Thomson's method of determining boric acid.

In conclusion, the author would like to acknowledge his indebtedness to Messrs. Cadbury Bros., Ltd., Bournville; Messrs. J. S. Fry & Sons, Ltd., Bristol; Messrs. Rowntree & Co., Ltd., York; the Scottish Federation of Grocers, and others who kindly supplied him with the samples necessary for this investigation.

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## The Separation of Vanadium from Tungsten.\*

By S. G. CLARKE, B.Sc., A.I.C.

(Read at the Meeting, May 4, 1927.)

THE usual procedures for determining vanadium in steels containing tungsten as a constituent involve the removal of the tungsten as the trioxide, the vanadium being determined in the solution. It has been found, however, that the tungstic oxide retains an appreciable amount of vanadium, the more so as the percentages of vanadium and tungsten increase, especially if the steel solution has been intentionally or accidentally evaporated to dryness. Thus, from a steel containing 18 per cent. of tungsten and 1 per cent. of vanadium, the separated tungsten oxide may contain 6 per cent. of the total vanadium. The problem to be dealt with was the determination of this quantity of vanadium retained by the tungstic oxide, or preferably, to avoid errors of separate analyses, merely its separation in a form in which it could be united with the main steel solution.

There appears to be no suitable process already recorded, although mention must be made of two early papers on the subject; one by Friedheim (*Ber.*, **23**, 353), who claimed to have effected a separation by the action of hydrochloric acid on the mixture of mercury salts of vanadic and tungstic acids, the other that of Browning and Goodman (*Z. anorg. Chem.*, 1897, **13**, 427; *Amer. J. Sci.*, (IV), **2**, 355) on the determination of vanadium in the mixture by reducing it in acid solution with tartaric or other hydroxy acids and subsequent iodimetric titration. These authors, who cite no results for small quantities of vanadium, note the interference of molybdenum in their method in its ordinary form, thus rendering it further inapplicable to the present problem should the steel contain molybdenum

\* Communication from the Research Department, Woolwich.

as a constituent, as this element is known to be partly retained by tungstic oxide in steel analysis.

**PRECIPITATION WITH CUPFERRON.**—Turning to the precipitation of vanadium by cupferron (the ammonium salt of nitrosophenylhydroxylamine), it was found that, although it is an accurate method when applied to solutions of vanadium alone, under the conditions of acidity of solution prescribed by Rodeja (*Anal. Fis. Quím.*, 1914, **12**, 305) and by Turner (*Amer. J. Sci.*, 1916, **41**, 339), the statement by Lundell and Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 344), that tungsten interferes, was confirmed. For example, on applying the cupferron method to a solution containing 0.2 grm. of tungsten, 0.007 grm. of vanadium, and 1 per cent. of free hydrochloric acid, somewhat less than half this vanadium was recovered. As there was only a slight turbidity, due to separated tungstic oxide, after adding the 1 per cent. of free hydrochloric acid, the low result could hardly be explained by the removal of vanadium from solution, but rather seemed due to the existence in solution of a complex unacted upon by cupferron. Addition of various reagents (ammonium tartrate, ammonium phosphate, borax) to similar vanadium and tungsten solutions did not lead to a quantitative precipitation of vanadium. By the addition of 10 c.c. of hydrofluoric acid to an almost neutral solution containing tungsten, vanadium and cupferron, a result was obtained which, although low, was sufficiently good to justify further work in this direction. Experiments were tried with varying amounts of both hydrofluoric and hydrochloric acids in the solution. The main results showed that, although enough hydrochloric acid must be present to ensure the precipitation of all the vanadium in presence of hydrofluoric acid, yet too much of the former acid may prevent quantitative precipitation. As regards the quantity of hydrofluoric acid allowable; increased amounts did not seem to lead to low results, but, as will be seen from the results given in the table marked with an asterisk, the quantity must not be reduced below a stated amount depending on the tungsten present, otherwise the detrimental influence of this element will come into play.

**TEST EXPERIMENTS.**—In the light of these general results, experiments were carried out to test the degree of accuracy obtainable; for this purpose comparatively large amounts of vanadium were taken, as well as the smaller quantities likely to be present in an impure tungstic oxide from steel analysis. A solution of known vanadium content was prepared by dissolving pure ammonium vanadate in sulphuric acid and diluting with water; this was checked by the usual sulphurous acid reduction and subsequent titration with permanganate standardised on sodium oxalate, the rose pink colour persisting for 30 seconds at 70° C. being taken as the end point. In all cases the content as calculated from the permanganate titre was used for comparison of results. Tungsten was added to the experimental solutions as a solution of sodium tungstate prepared by dissolving a known weight of tungstic oxide in sodium hydroxide solution and boiling to give the normal tungstate. Known amounts of these solutions were mixed and diluted to about 300 c.c.; the stated amount of hydrofluoric acid was then added from a glass

measure (the interior of which had been waxed), and the solution approximately neutralised with ammonia. After the addition of the stated amount of hydrochloric acid (sp. gr., 1.2), a solution of 1 gm. of cupferron in about 20 c.c. water was stirred in. If the solution was more than slightly warm it was allowed to cool before the addition of these last two reagents. The precipitate of the cupferron compound appeared at once as a fine brown powder, changing rapidly in colour to yellow. It was filtered off, after 15 minutes, on a pulp filter, washed with dilute cupferron solution containing a few drops of 1:3 sulphuric acid and burnt off in a platinum dish. If the ignition was conducted at a low temperature, the vanadium pentoxide remained unfused, and in this condition was fairly readily dissolved out of the dish by the addition of a small volume of concentrated sulphuric acid and heating; it was then determined by diluting with water to about 200 c.c., adding 20 c.c. of saturated sulphur dioxide solution, boiling steadily for 20 minutes, and titrating with 0.1 *N* permanganate solution at 80° C. For the smaller amounts one-fiftieth normal permanganate was used. If the burning off of the cupferron precipitate was finished at a dull red heat, the oxide fused to a dark red crystalline mass, and it was then found quicker to bring it into solution by fusing with a few grms. of fusion mixture, with subsequent solution in water; this solution, after filtration and acidification with sulphuric acid, was reduced and titrated as above. Preliminary oxidation with permanganate before the reduction with sulphurous acid was not usually done, as it was found to be without influence on the results. The table gives some results obtained.

Vanadium. Grm.	ADDED. Tungsten. Grm.	In 300 c.c. of solution		FOUND. Vanadium. Grm.
		HCl. C.c.	HF C.c.	
0.0074	Nil	6	3	0.0070
0.0074	0.2	6	3	0.0075
0.0502	Nil	10	3-5	0.0500
0.0502	0.2	10	3-5	0.0500
0.0100	0.2	10	3-5	0.0099
0.0502	1.0	10	3-5	0.0490*
0.0251	1.0	10	3-5	0.0209*
0.0251	1.0	20	10	0.0251
0.0251	1.0	30	15	0.0247
0.0200	0.2	20	10	0.0204
0.0050	1.0	20	10	0.0052

\* *Vide supra*

From the table it will be seen that good results for vanadium in solution in presence of moderate and large amounts of tungsten may be obtained by the cupferron precipitation by adding 10 c.c. of hydrofluoric acid, neutralising with ammonia, then adding 20 c.c. of hydrochloric acid, diluting to about 300 c.c., and precipitating with cupferron, as described. Small amounts of vanadium require the addition of 50 grms. of ammonium chloride in the solution and a simultaneous increase in the amount of hydrochloric acid to 25 c.c.

APPLICATION TO IMPURE TUNGSTIC OXIDE FROM STEEL.—The impure tungstic oxide, as ordinarily separated from a steel, may be dealt with satisfactorily for the separation or determination of vanadium, by dissolving it in sodium hydroxide solution or ammonia and boiling to give the normal tungstate. The small quantity

of ferric hydroxide remaining undissolved is filtered off; as it contains a little vanadium, it is washed, dissolved in hydrochloric acid, and added to the main steel solution. The vanadium, now present with the tungstate in the filtrate, is recovered by the cupferron precipitation under the conditions already described. The vanadium pentoxide obtained is dissolved in sulphuric acid and added to the main steel solution, this method of treatment being preferred to the fusion with alkali carbonates, as the introduction of alkali salts may be undesirable in this solution.

Under the conditions of the experiments no action on the glass of the vessels was observed. No waxing or other treatment of beakers was found necessary.

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### Note.

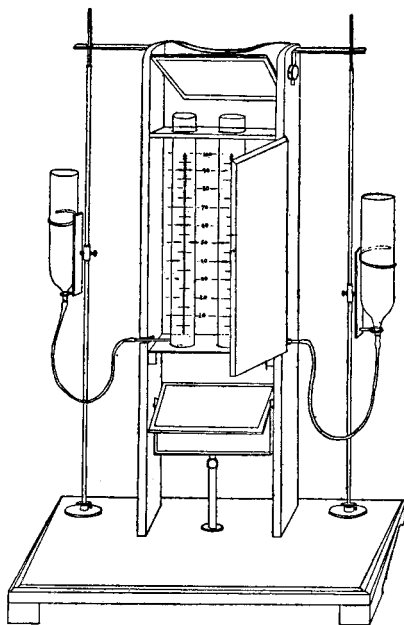
*The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.*

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#### A SIMPLE COLORIMETER.

THIS colorimeter was devised primarily for colour matching in my modification of the phenolsulphonic and sulphuric acid method for determination of nitrates in water (ANALYST, 1919, 44, 281). In this method the sample and the standard solution are finally made to 100 c.c. in measuring cylinders, and that which has the stronger colour is diluted to match the other; from this the result is calculated.

The difficulty of obtaining measuring cylinders sufficiently free from colour is the reason for one feature of this apparatus, namely, the use of colourless glass tubes, of exactly equal diameter, to which colourless glass discs have been attached, with a suitable adhesive, at one end to form cylindrical vessels. These cylinders have a side tube which is connected by means of a narrow rubber tubing with glass reservoirs held in a cradle on either side, as shown in the figure. The reservoirs can be moved freely up and down by sliding the cradles on the metal rods, and after the rough adjustment has been fixed by means of the screw at the side, a fine adjustment is made by turning the screw at the base of the metal rod. An adjustable mirror reflects light through the cylinders, and the colour images are observed on the upper mirror. To facilitate accurate comparison, the cylinders are only 3 mm. apart (in the figure this distance is exaggerated for clearness), and hence observation in the second mirror is necessary to avoid stereoscopic effect. The cylinders and reservoirs are easily removed for cleaning.



In using the apparatus the solution from the sample is poured into one reservoir, and that from the standard into the other. The capacity of the cylinders is such that 100 c.c. of solution reaches the 100 mark on the graduated scale, with a small quantity remaining in the reservoir and connecting tube. The two reservoirs can be moved up and down until the observed colour depths are approximately equal and are then finally adjusted. It is unnecessary to arrange for one solution to be at any exact point initially; when a match has been made the ratio is at once obtained by opening the door and reading the graduated scales on the back of the instrument. As the coloured liquids are not diluted, the colour intensity of either is not reduced irretrievably, as in the ordinary method of matching, and it is necessary to prepare only one standard.

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## 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.*

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### COUNTY OF ABERDEEN.

#### ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1926.

THE total number of formal samples analysed during the year was 254, of which 10 were reported to be adulterated, deficient or doubtful. An examination was also made of 335 informal samples of foods and drugs.

**CONDENSED MILK.**—Eight samples examined complied with the Regulations. To determine the effect of standing for a prolonged period on the uniformity of composition a tin of unsweetened condensed milk was left for several months, and its contents then divided, as carefully as possible, into three layers. In the bottom layer the fat was only 2 per cent., whilst the middle and upper layers contained 12 and 20 per cent., respectively. The lowest layer contained much crystallised sugar.

**HONEY.**—A sample of honey was found to contain 7 per cent. of sucrose, an unusual amount. The sample also contained 21 per cent. of dextrose, 25 per cent. of laevulose, and 2 per cent. of mannite. Notwithstanding its high sucrose content, I regard it as genuine honey.

**BYRE SAMPLES OF MILK.**—(a) *Daily Variations in the Proportions of Butter Fat in the Milk from Single Cows and from Herds of Cows.*

When formal samples are found to be below the prescribed presumptive limits in butter fat and solids-not-fat, sampling officers frequently take byre samples as soon as possible after the formal sample of milk has been reported on. Very often the byre sample is taken the day after the formal sample has been examined and found deficient. The assumption underlying the recommendation of the Board of Agriculture that byre samples should be taken is that the proportions of butter fat and solids-not-fat would be practically the same on succeeding days.

Of the 90 formal samples analysed, it was found that six samples were deficient in butter fat, and one sample was deficient in solids-not-fat. The percentages



were, respectively, 2.73, 2.78, 2.85, 2.95, 2.80, and 2.68 per cent., or deficiencies compared with the prescribed presumptive limit of 3 per cent. to the extent of 0.27, 0.22, 0.05, 0.20, and 0.32 respectively. The percentage of solids-not-fat in the one sample deficient in this group of constituents was 8.26, or 0.24 per cent. below the prescribed presumptive limit of 8.5 per cent. Byre samples from individual cows revealed the fact that in one case two out of six cows were giving poor milk. The figures were respectively 2.91, 3.90, 3.28, 1.98, 3.12, and 3.90. It should be pointed out, however, that unless the yield from each cow is also given, the percentage of butter fat for the bulked milk cannot be found. The samples sent to the Analyst were samples of equal bulk (approximately 8 ounces). Cows giving rich milk usually give smaller yields than the average, and cows giving poor milk usually give larger yields than the average. Occasionally, however, a cow giving rich milk gives a large yield, but this is exceptional. In all cases, therefore, where byre samples are taken, the yield of each cow should be noted.

A number of morning and evening samples from herds of cows within the county were, therefore, analysed in order to ascertain the extent of the variations, if any, in the percentages of butter fat and solids-not-fat in daily samples of individual cows and also in the bulked milk of the same herd. The following table shows the percentages of butter fat and yield from five single cows and from the bulked milk of five cows, from a herd of good cows:—

SHOWING THE DAILY VARIATIONS IN THE PERCENTAGES OF BUTTER FAT, SOLIDS-NOT-FAT, AND YIELD IN INDIVIDUAL COWS AND IN A HERD OF FIVE COWS.

	COW No. I.				COW No. II.				COW No. III.			
	MORNING.		EVENING		MORNING.		EVENING.		MORNING.		EVENING.	
	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.
First day	19.00	3.15	11.00	3.45	17.00	3.40	7.25	3.38	9.00	4.95	9.00	4.90
Second day	20.00	2.80	14.00	3.15	16.50	2.83	11.00	3.15	10.25	5.20	9.25	5.10
Third day	17.00	2.70	7.50	3.45	14.00	5.30	6.25	3.30	10.00	3.45	7.50	5.40
Fourth day	19.00	2.10	9.00	3.70	16.50	2.90	6.25	3.35	9.25	4.80	10.00	5.00
Fifth day	10.75	1.30	9.75	3.95	16.50	3.08	7.00	3.45	11.75	4.60	10.00	4.70
Sixth day	7.75	5.40	11.25	4.10	14.00	2.90	7.00	3.35	11.25	4.55	11.25	5.30
Seventh day	13.50	2.75	13.00	3.50	15.75	2.75	7.50	3.35	12.25	5.50	10.25	4.80
Eighth day	13.25	3.85	12.50	3.30	12.25	2.95	7.50	4.50	9.75	4.60	10.00	4.50
Ninth day	16.50	4.50	14.50	3.08	13.25	4.35	9.25	3.15	9.50	3.15	10.00	4.85
Tenth day	14.50	3.20	5.50	3.25	12.25	3.25	9.50	3.27	9.75	4.63	9.50	4.70
Eleventh day	19.00	3.42	17.25	3.32	14.50	3.37	7.50	3.90	9.50	4.80	9.00	5.00
Twelfth day	18.50	3.50	—	—	13.50	3.35	—	—	9.50	4.85	—	—

Per cent.	COW No. I.		COW No. II.		COW No. III.							
bulk milk	15.73	3.22	11.39	3.48	14.67	3.37	7.82	3.47	10.15	4.59	9.61	4.93

	COW No. IV.				COW No. V.				ALL COWS.			
	MORNING.		EVENING		MORNING.		EVENING.		MORNING.		EVENING.	
	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.	Yield. Pounds.	Per-centage.
First day	16.00	5.32	10.25	5.37	21.00	3.45	12.00	3.58	16.4	4.05	9.9	4.14
Second day	17.25	5.10	9.00	5.65	21.50	3.22	9.00	3.50	17.1	3.83	10.5	4.11
Third day	17.00	5.55	9.50	5.75	21.00	3.20	11.50	3.30	15.8	4.04	8.5	4.24
Fourth day	17.00	4.80	8.75	6.30	21.00	3.10	10.25	3.85	16.6	3.54	8.9	4.44
Fifth day	17.00	5.10	10.50	6.45	20.25	3.00	10.50	3.70	15.3	3.42	9.6	4.45
Sixth day	16.75	5.10	8.25	6.20	19.75	3.25	11.50	3.50	13.9	4.24	9.9	4.49
Seventh day	17.00	5.10	10.25	6.25	21.25	3.20	10.50	3.65	16.0	3.86	10.3	4.31
Eighth day	17.50	4.70	9.75	5.25	20.50	3.05	11.25	3.50	14.7	3.83	10.2	4.21
Ninth day	17.00	2.95	9.25	5.40	21.00	2.75	11.50	3.65	15.5	3.54	10.9	4.03
Tenth day	13.50	4.40	9.25	6.00	19.75	3.22	10.25	3.70	14.0	3.74	8.8	4.19
Eleventh day	17.25	4.25	8.50	5.45	20.75	3.15	11.00	3.55	16.2	3.80	10.7	4.25
Twelfth day	17.25	3.90	—	—	21.00	3.25	—	—	16.0	3.77	—	—

Per cent.	COW No. IV.		COW No. V.		ALL COWS.							
bulk milk	16.71	4.69	9.39	5.82	20.73	3.15	10.84	3.59	15.63	3.81	9.84	4.26

In all cases the cows were thoroughly milked dry, that is to say, each cow was stripped. It was thought necessary to do this in order to find out the true yield of butter fat. In ordinary dairying practice, however, each cow is not milked absolutely dry, and therefore the proportions of butter fat would be lower than in the case of cows completely stripped.

The following table shows the results of analyses for butter fat of daily samples of the bulked milk from eight cows for 21 days:—

Butter fat.	DAY.										
	1st.	2nd.	3rd.	4th.	5th.	6th.	7th.	8th.	9th.	10th.	11th.
Morning, per cent.	3·64	3·25	3·48	3·49	3·44	3·10	3·40	3·36	3·25	3·11	3·36
Evening, per cent.	4·23	4·08	4·24	3·91	4·34	4·46	4·20	3·76	4·06	4·04	3·65

Butter fat.	DAY.										
	12th.	13th.	14th.	15th.	16th.	17th.	18th.	19th.	20th.	21st.	Avg.
Morning, per cent.	3·08	2·98	3·24	3·15	3·45	3·50	2·89	3·23	2·84	3·14	3·26
Evening, per cent.	3·99	3·90	3·90	3·58	3·65	3·44	4·19	4·29	3·80	4·05	3·99

These results prove how extremely difficult it is to judge *from a byre sample alone* whether the official sample of the previous day is or is not likely to be a sample of genuine milk. The variations would be further accentuated by the degree of incompleteness of the milking of each cow, as the latter portions of the milking are much richer in butter fat than the first portions. Thus the obvious duty of the dairyman is to select his cows so as to provide that the lowest percentage of butter fat never falls below 3 per cent. in the bulked milk.

(b) *Sampling of Milk.*—In view of the fact that there have been Court cases arising out of the sampling of milk in glass bottles, informal samples of milk in pint bottles from the county were analysed, with the object of determining the variations in the percentage of butter fat due to difference in methods of sampling. It had been asserted in Court that it was sufficient to give a slight shaking to a pint bottle full of milk in order to ensure uniform distribution of the butter fat prior to the sample being divided into the necessary three parts. Altogether, six samples of milk in pint bottles were taken and each was divided into three parts, the treatment as to sampling being different for each of the six samples. There were thus 18 parts of milk to be analysed. Samples I, II and III were evening milk bottled in the morning, and delivered five hours after bottling. Samples IV, V and VI were morning milk, delivered four hours after bottling. Samples I and IV were poured into a sample container after the bottles had been well shaken, and each sample was divided into three parts, (a) being the first part, from the top, (b) the second part, from the middle, and (c) the third part, from the bottom. Sample No. II was submitted to slight shaking, according to the description given in Court—a few up and down movements. Samples III and VI were not shaken at all, but were just divided into three parts from the bottles. Sample No. V was turned upside down quite sharply three times. The following table shows the results of analyses of the three parts (a), (b) and (c) of the six samples:—

PERCENTAGE OF BUTTER FAT.						
Parts.	I.	II.	III.	IV.	V.	VI.
A. Top ..	3·50	6·40	7·48	3·63	3·82	6·57
B. Middle ..	3·55	2·71	2·14	3·61	3·58	2·64
C. Bottom ..	3·48	1·38	0·93	3·62	3·45	1·62

It will be seen that the three parts of the samples I and IV, which were removed from the bottles after shaking and thoroughly mixed in a container, had the butter fat uniformly distributed throughout. Sample No. II which was only slightly shaken before being divided into three parts, showed marked differences in the three parts, the upper part naturally containing most butter fat (6.4 per cent.) and the lowest part the least (1.38 per cent.). Samples Nos. III and VI, which were not shaken at all, showed high proportions of butter fat at the top and low proportions at the bottom. Sample No. V which received sharp up and down movements, showed a higher proportion of butter fat at the top and a lower proportion at the bottom. The difference between the upper and the lower layer amounted only, however, to 0.37 per cent. of butter fat. The difference in percentage in sample No. III between the top part and the bottom part amounted to 6.5 per cent. of butter fat. The results show that, when formal samples are taken of milk sold in pint or quart bottles, the milk should be removed from the bottle and placed in a sample container and stirred, put back into the bottle, and again returned to the container and stirred, before being divided into three parts. By this process each of the three parts should contain the same proportion of butter fat. Any method of sampling by shaking the milk in the bottle is quite unsatisfactory, and should not, therefore, be practised by the sampler. There is no assurance that such sampling will secure that the proportions of butter fat in each of the three parts will be the same. The samples were delivered from a milk cart after a considerable journey, and when they arrived in the laboratory each of the bottles had a considerable layer of cream at the top. The jolting of a cart is not sufficient to ensure that the milk is uniformly distributed in a full glass bottle before delivery to a customer.

**ESSENCE OF RENNET.**—Samples of essence of rennet were examined for the presence or absence of boric acid, as, under the new Regulations boric acid is prohibited in essence of rennet supplied for sale, as a curdling agent of milk, to the public. Samples were found to contain from 1.7 per cent. to 2.1 per cent. of boric acid. It is doubtful whether the use of boric acid as a preservative for concentrated rennet used in cheese-making can be prohibited. Boric acid is an excellent preservative, and is easily washed out in the process of cheese-making.

**ASTHMA CIGARETTES.**—Several samples of asthma cigarettes were examined, and were found to be prepared from stramonium leaves and potassium nitrate. Powders used for relieving asthma contained stramonium, Indian hemp, and powdered potassium nitrate, with a little flavouring in the form of eucalyptus oil.

J. F. TOCHER.

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## CITY OF BIRMINGHAM.

### REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1927.

OF the 1541 samples examined during the quarter, 1308 were submitted under the Food and Drugs Acts. These comprised 1252 informal samples (29 adulterated) and 56 formal samples (6 adulterated). The adulterated samples were 22 milks, 5 butters, 3 baking powders, 2 seidlitz powders, and 1 margarine (preservatives only).

**CONDENSED MILK.**—Six informal samples of *full cream* milk contained from 31.5 to 36.6 per cent. of milk solids, of which 8.9 to 9.9 per cent. were milk fat. One of the samples was thus slightly low in fat. Another sample directed that one part of milk should be added to three or four parts of water, without "clearly

specifying that the liquid so produced was not of equivalent composition to milk." The attention of the manufacturers was called to the incomplete statement.

**BUTTER.**—Seventy-seven per cent. of the 186 samples were free from boric acid, 20 per cent. contained 0·1 per cent., and 3 per cent. from 0·2 to 0·3 per cent.

**ALE AND BEER.**—Six samples of beer and 3 samples of ale were free from arsenic and preservatives, and did not contain an excess of common salt. According to the Preservatives Regulations, beer may contain 70 parts of sulphur dioxide per million, but no mention is made of ale. One of the Finance Acts has a definition of "beer," which includes ale, porter, etc., but that definition is expressly stated to apply to the second part of that Act, and I am not aware of any general definition of beer which would include ale, etc. Strict interpretation of the Regulations, therefore, would require that no sulphur dioxide should be present in ale, but it appears to be reasonable to allow the same proportion in ale as in beer.

J. F. LIVERSEGE.

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## 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.*

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### APPLICABILITY OF WARRANTY.

ON June 12 a tradesman was summoned at Rathdrum by the Wicklow County Council for the sale of adulterated butter to a County Home, of which he was the contractor. Evidence was given that a sample of the butter had been analysed and found to be deficient in butter fat and to contain 23·29 per cent. of water.

Mr. Cullen, solicitor for the defence, said that his client had a warranty for this butter from a wholesale Dublin firm, and would give evidence that the butter was delivered as received and had not been tampered with in any way.

The solicitor for the County Council said that it had been decided that a warranty, to be effective, must be received direct from the vendor, whereas in this case it had been delivered to the defendant's wife.

To this Mr. Cullen replied that he thought that it was stretching technicalities too far to deprive his client of a proper legal defence in this way. The wife had simply acted as agent in the matter, and the butter had been paid for by the defendant's money.

Counsel for the prosecution, however, replied that if they had not been satisfied that the wife was the actual purchaser, he would not have raised the point, but he contended that she was in the position of a third person receiving a warranty; she was not the person from whom the sample was taken and she was not the defendant in the case. All the receipts and warranties had been made out in her name, and all correspondence had been between her and the wholesale firm.

A representative of the wholesale firm stated that 23 per cent. of moisture was so abnormal that he had come specially to give evidence as to the butter which they had supplied to this lady. In his opinion something had happened to the butter after leaving their premises.

The Justice decided that the defendant could not rely on the warranty. He imposed a fine of £2 with £1 costs, and allowed five guineas expenses to the representative of the wholesale firm, and 19s. 6d. as the Analyst's fee.

## POLLUTION OF A RIVER WITH COLLIERY BY-PRODUCTS.

MAWSTON *v.* PEASE AND PARTNERS.

IN this case, heard at the Durham March Assizes, before Mr. Justice Fraser, the plaintiff, a farmer, claimed an injunction to restrain the defendants from polluting the River Skerne with the effluents from the Chilton and Fishburn Collieries, and also damages against them for loss of cattle and contamination of pastures.

Evidence was given by Mr. C. J. H. Stock, that he had analysed the water in September, 1925, and had found that the sample indicated considerable industrial pollution. The water contained a considerable proportion of phenol and tar bases, which ought not to be there. On February 16, 1927, he had taken samples from this stream, and had found that the water was not pure, though it compared favourably with the water above where the Chilton Colliery effluent joined the stream. That was, there were other sources of pollution.

Dr. Geoffrey Martin said that he had analysed the water from the stream at four different points. The sample of No. 2 effluent, from the coke oven plant as it entered the stream, contained 30.6 parts of tar acids, 7.75 parts of tar bases, and 3 parts of neutral oil per 100,000. The free ammonia was 8.2, and the oxygen absorption 82.04. In his opinion such an effluent discharged into a stream would cause pollution and was unfit for cattle to drink.

A sample from the stream, 150 yards lower down, still showed the presence of tar products in injurious amounts, and had a high oxygen absorption value.

The mud contained growths similar to those which flourished in sewage waters, and showed a high content (21 parts per 100,000) of tar oils, which would be dangerous to cattle entering the stream and stirring up the mud.

Professor Wooldridge, for the defence, said that, in his view, the death of the animals could not have been caused in the way suggested, since the quantities of phenols, etc., were too small. In his opinion, the *post-mortem* appearances were more consistent with death from parasitic disease than with death from phenol poisoning, and he stated that he had found that the low lying land in the vicinity of the stream was prolific in parasites. He did not agree with the evidence of a veterinary surgeon called for the plaintiffs, who was quite certain that the lesion in a cow was not parasitic in its origin.

Mr. Justice Fraser, in his judgment, said that experts were very helpful up to a point, but that they merely endeavoured to guide a judge or a jury by their opinion and their experience. It remained for the jury or the judge to decide, as best they could, a question of fact when the opinions of experts differed. In such a case as the present, for instance, where the opinions of the expert witnesses differed *toto coelo* from one another, all one could do was to apply one's own knowledge of the world, and one's knowledge (such as it might be) of a limited nature, to the particular matters upon which the witnesses might give evidence.

After summarising the evidence, the Judge first made some observations about the law. A person had at Common Law, he said, no right to pollute water, so that in a polluted state it passed to the land of another person who had the right to receive the water. When water was polluted it was not necessary that the person who had the right to complain of the pollution should prove that he had suffered actual damage before the Courts would interfere to protect him. It was sufficient to prove that his right to have the water flow to him in its natural state had been infringed.

Two cases might be cited as authorities, namely, *Crossley & Sons, Ltd., v. Lightowler* (1867, 2 Chancery Appeals, p. 478) and *Jones v. The Llanrwst Urban Council* (1911, 1 Chanc., p. 393). In the former case it was held that "A person

may pour matter into water, which by itself may not cause pollution, and other persons may do likewise, yet if the combined effect is to cause pollution, each of them may be restrained by injunction, and it is no defence to action to restrain for pollution, that others also fouled the water."

The Judge found, as a fact, that the death of a cow on August 31st, 1925, was caused by the act of the defendants, who polluted the water. With regard to the claim for the alleged losses of other cows, and horses, the plaintiff had not satisfied him that the defendants had caused these deaths, or that they had caused the abortion of calves. He was satisfied that there was pollution of the stream, and that it was still going on, and therefore granted the injunction claimed. He allowed the plaintiff the general costs of the action, and allowed defendants such costs as related exclusively to the issues in which the plaintiff had failed.

It was agreed that there should be a stay of six months before the injunction took effect, subject to the defendants indemnifying the plaintiff from any loss.

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### SULPHUR DIOXIDE IN PEARL BARLEY.

ON June 28, a Lambeth grocer was summoned at Old Street Police Court by the Bethnal Green Borough Council for having sold pearl barley which contained 90 parts per million of sulphur dioxide.

Mr. R. A. Beck, for the defence, submitted that there could be no conviction of a defendant under the Preservatives Regulations unless the Court was satisfied that he had wilfully neglected to carry out the regulations. These goods were purchased in February from a reputable firm, with a guarantee, and with that guarantee it could not be submitted that there had been wilful neglect with regard to the regulations. The defendant knew nothing about the regulations, and the first intimation he had had that anything was wrong was the receipt of the summons. Mr. Beck observed that, in his view, these proceedings were premature and misconceived, because representations had been made to the Ministry of Health which had been favourably regarded.

The Magistrate (Mr. Snell) said that the amount of sulphur dioxide in the barley was so small, taking into consideration the fact that other commodities were allowed to contain various quantities much in excess of the amount, that it seemed to him that this was one of the most trivial cases, based on the smallest possible offence against the regulations that could be conceived. There were two alternatives. He could dismiss the summons on payment of costs, or discharge the defendant under the Probation of Offenders Act. He dismissed the summons on payment of £2 2s. costs.

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## United Provinces of Agra and Oudh and the Central Provinces.

### ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1926.

ACCORDING to the Report of the Chemical Examiner, Mr. D. N. Chatterji, the total number of cases reported on was 1538, a decrease of 384 on the previous year (ANALYST, 1926, 51, 349), but the medico-legal cases numbered 1141, as compared

with 1068 in 1925. Suspected human poisoning cases showed an increase from 394 to 398, and blood-stain cases increased from 616 to 676, whilst cattle poisoning cases decreased from 47 to 34. The decrease in the total number of general chemical analyses was due to the smaller number of excise cases, such cases being now mainly referred to the Chemical Examiner for Customs and Excise, Calcutta.

**BLOOD AND OTHER STAINS.**—Of the 923 specimens of stains examined, 677 were sent to the Imperial Serologist, Calcutta, for tests as to their origin. In 116 cases the origin could not be determined, owing to disintegration or to the amount being insufficient, 8 were found to be the blood of a ruminant animal, 2 were non-mammalian blood, 2 were both human and non-mammalian blood, and 5 were seminal stains of human origin; in 4 stains no blood could be detected.

**TESTS FOR COCAINE.**—During the year tests for the presence of cocaine were applied to 234 substances, a decrease of 329 on the previous year. In 164 cases impure cocaine was present, in 37 cases the cocaine was mixed with antipyrin, and in 10 cases with benzoic acid. Cocaine was absent in 11 cases.

**HUMAN POISONING.**—Of the 332 specimens of viscera, vomit, etc., examined poison was detected in 120. Opium was found in 46 exhibits, arsenic in 76, datura in 61, alcohol in 1, glass in 2, and strychnine in 2. Poisons were also detected in 203 miscellaneous articles submitted. In a case from Gorakhpur a man died, presumably of typhoid fever, after 3 days' illness, and his body was cremated. In addition to delirium, the patient had vomiting and purging during his illness, and owing to suspicions which arose, washings from the floor on which the deceased had vomited were submitted for chemical examination. Arsenic was detected in these.

In a case of suspected abortion a piece of wooden stick submitted for examination was found to be smeared at one end with a substance in which *Plumbago zeylanica* (used as an abortifacient) was detected.

**CATTLE POISONING.**—Arsenic was detected in the 7 exhibits of viscera or excreta, and poisons were found in 44 miscellaneous articles, including yellow oleander in 29, *Abrus precatorius* in 2, arsenic in 7, hydrocyanic acid in 2, and opium, aconite, *Nux vomica*, and *Plumbago* in 1 exhibit each.

In a case from Jodhpur about 95 cattle and 2 goats were affected by eating two bundles of *Juar kadvi*. The remnants of the two bundles were found to contain 0.0112 and 0.0073 per cent. of hydrocyanic acid. The development of the hydrocyanic acid from the cyanogenetic glucoside in the plant was attributable in this case to a failure of rain in Marwar, owing to which the kadvi had dried up prematurely.

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## City of London.

### REPORT OF THE MEDICAL OFFICER FOR THE YEAR 1926.

The Annual Report of the Medical Officer of Health (Dr. W. J. Howarth) gives the usual statistical information about the city area and its population (*cf.* ANALYST, 1926, 51, 412), including statistics of infective diseases, etc.

**SMOKE AND ATMOSPHERIC POLLUTION.**—The results obtained by the Public Analyst (Mr. E. A. Pinchin) are summarised in a table showing the rainfall for the months from January to December, and the amounts of insoluble matter (tar soot and dust) and soluble matter, together with the sulphates, ammonia and chlorine. The results, which have been re-calculated into metric tons per sq.

kilom., show that in the month of November, only, the amount of deposit registered as falling in the City was 28.77 tons per sq. kilom., which is equal (taking the area of the City as 1 sq. mile) to 73 tons avoirdupois. Of this, approximately 41 tons were soluble, and 32 tons were insoluble, consisting of tar, carbon and grit. The variation in the amount of impurity in the air at noon from Jan. 1st to Dec. 31st varied from 0.5 to 6 mgrms. per cb. ft. of air, the larger figure including times when there was a fog.

**SUPERVISION OF FOOD AND DRUGS.**—During the year 1048 samples were submitted to the Public Analyst, of which 686 were informal samples (18 adulterated) and 362 were formal (27 adulterated). Ten samples of drugs did not comply with the requirements of the B.P. There was one prosecution, the vendor of liniment of turpentine, which was deficient to the extent of 57 per cent. in turpentine, being fined £5 and costs. In other cases cautions were issued.

**BUTTER ON BREAD.**—Of the 113 samples of butter taken, 64 were of butter served with bread or scone. Of these samples, 5 were found to consist of margarine. Prosecutions were instituted in two cases and in each case fines were imposed.

**MILK SAMPLED AT RAILWAY STATIONS.**—Samples despatched from 42 different farms were collected on arrival at Liverpool Street and submitted to the City Bacteriologist (Sir F. Andrewes), who reported that 28 of them could be passed as clean, whilst the remainder contained only traces of dirt. For the first time since 1913 no tuberculous milk was found among the samples taken.

**CANNED LOGANBERRIES.**—Attention was directed to a problem connected with the canned food industry by the surrender, in one of the Metropolitan Boroughs, of a quantity of tins of loganberries which were assumed to be unsound on account of their "blown" condition. It has been observed that with loganberries or other fruits containing "pips" (such as raspberries), that the tins in which they are contained may first show the desirable concavity at the ends, and accordingly be passed as sound, but after a few months, whilst the contents should still be sound—and, moreover, generally are sound—the concavity is replaced by a convexity and a suspicion of unsoundness is aroused. When opened, the contents of the tins, so far as the usual criteria of taste and smell are concerned, show no decomposition changes to account for the gas production which had undoubtedly taken place.

Six tins of loganberries showing convex ends and apparently "blown" were examined by the City Bacteriologist. The contents were nearly, but not quite, sterile on culture. None of the anaerobic cultures yielded any growth. Of five aerobic cultures, two were sterile, one showed 6, and the other 3 colonies. The bacteria, chiefly bacilli, were of various kinds, probably came from the contents of the tin. The "blown" character of the tins could not be attributed to bacterial action.

A chemical examination was made by Mr. E. A. Pinchin, who found that on opening one of these tins a distinct gas pressure was observed; and after a short time bubbles rose to the surface. The contents of the tin contained 0.20 per cent. of absolute alcohol by weight. The "blowing" was therefore attributable to a slight alcoholic fermentation.

In view of the Public Analyst's report, the circumstances were communicated to the Ministry of Health in the hope that the manufacturers concerned might be induced to undertake research with the object of reducing the probability of such alcoholic fermentation. Unless some such action is taken, it is certain that manufacturers will suffer from more or less extensive condemnations of a product which does not deserve condemnation.



# Ministry of Health.

## STATUTORY RULES AND ORDERS, 1927, No. 577.\*

### PUBLIC HEALTH, ENGLAND.

THE PUBLIC HEALTH (PRESERVATIVES, &C., IN FOOD) AMENDMENT REGULATIONS, 1927, DATED JUNE 25, 1927, MADE BY THE MINISTER OF HEALTH.

71,855.

The Minister of Health, in the exercise of the powers conferred upon him by the Public Health Act, 1875, the Public Health (London) Act, 1891, the Public Health Act, 1896, the Public Health (Regulations as to Food) Act, 1907, and the Butter and Margarine Act, 1907, and of every other power enabling him in that behalf, hereby makes the following Regulations, with the consent of the Commissioners of Customs and Excise, so far as they apply to the Officers of Customs and Excise.

1. These Regulations may be cited as the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1927; and these Regulations and the Public Health (Preservatives, &c., in Food) Regulations, 1925 (hereinafter called "the principal Regulations"), and the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1926 (hereinafter called "the Regulations of 1926"), shall be construed together and may be cited together as the Public Health (Preservatives, &c., in Food) Regulations, 1925 to 1927.

2. The principal Regulations as amended by the Regulations of 1926 shall be further amended as follows:—

(1) The words "manufacture for sale or" shall be inserted after the words "prohibit the" in the first line of proviso (ii) to Article 1.

(2) The following proviso shall be added to Article 1:—" (iii) the Regulations shall not apply to the sale of pearl barley until the 1st day of January, 1928."

(3) In the definition of "preservative" contained in Article 2 (1) the words "lactic acid" shall be inserted after the word "sugars."

(4) The words "any added colouring matter being one of those" shall be substituted for the words "any of the colouring matters" in Article 4 (1) and Article 11 (1).

\* H.M. Stationery Office. Price 1d. net.

(5) The words "otherwise than in item 4 thereof" shall be inserted after the word "Schedule" in the second line of proviso (ii) to Article 4 (1) and in the second line of proviso (ii) to Article 11 (1).

(6) The following additional proviso shall be inserted at the end of Article 4 (1) and at the end of Article 11 (1)—" (iii) The provisions of this Article shall not apply so as to prohibit the presence of sulphur dioxide in any article of food other than meat if it is shown either—(a) that the article not being an article specified in Part I of the said Schedule is intended to be used in the preparation of an article which is so specified, or (b) that the article being itself an article so specified, other than fruit or fruit pulp, is intended to be so treated before it is sold or exposed for sale by retail as to comply with the provisions of the Schedule as regards the proportion of sulphur dioxide contained."

(7) In Part I of the First Schedule for the item numbered 8 there shall be substituted the following items—

Food.	Preservative.	Parts per million.
8. Sugar (including solid glucose) and cane syrups.	Sulphur dioxide ..	70
8a. Cornflour (maize starch) and other prepared starches.	Sulphur dioxide ..	100

Given under the Official Seal of the Minister of Health this Twenty-fifth day of June, in the year One Thousand nine hundred and twenty-seven.

(Signed) H. W. S. FRANCIS

(Assistant Secretary, Ministry of Health).

\* H.M. Stationery Office. Price 1d.

PUBLIC HEALTH (PRESERVATIVES, &c., IN FOOD) AMENDMENT  
REGULATIONS, 1927.\*

CIRCULAR 806.

*(Issued to Authorities administering the Food and Drugs Acts.)*

SIR,

1. I am directed by the Minister of Health to refer to the second paragraph of Circular 782 of the 14th April, 1927, and to forward for the information of the Authority a copy of the Public Health (Preservatives, &c., in Food) Amendment Regulations, 1927, which take the place of the provisional Regulations dated 8th April, 1927. It will be observed that the new Regulations reproduce the provisional Regulations and incorporate in addition a few minor amendments of the principal Regulations.

2. Representations have been received to the effect that there are in this country stocks of hams and bacon preserved by borax which were imported before the 1st June but, owing to unforeseen circumstances, cannot be disposed of before the 1st July, the date on which the Regulations come into operation as regards those articles. After considering these representations, the Minister thinks that the case will be met if Local Authorities will follow the course suggested in paragraph 3 of Circular 751 and not institute legal proceedings in respect of old stocks of hams and bacon during the next few months where they are satisfied that reasonable efforts have been made to clear such stocks and that further consignments will conform with the Regulations.

3. The Minister desires to draw the attention of Local Authorities to the fact that traces of some of the prohibited preservatives and colouring matters are naturally present in certain foods, *e.g.* boric acid and benzoic acid in some fruits, and copper in peas and other vegetables. The quantities so present are usually insignificant, being much less than those which would be required for effective preservation or artificial colouring. What the Regulations prohibit is the importation, manufacture or sale of articles of food containing *added* preservative or colouring matter. It would, therefore, appear to be desirable that Local Authorities, before instituting legal proceedings in respect of the presence of small traces, should satisfy themselves that the circumstances are such as to afford *prima facie* grounds for the assumption that the prohibited substances have been artificially introduced.

4. Copies of this Circular and of the amending Regulations are being sent to the Medical Officer of Health and the Public Analyst.

*(Signed)* R. B. CROSS  
*(Assistant Secretary).*

MINISTRY OF HEALTH,  
June 29, 1927.

\* H.M. Stationery Office. Price 1d.

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 ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.
 

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## Food and Drugs Analysis.

**Properties of Maize Starch. Removal of Combined Fatty Acids.**  
**T. C. Taylor and J. H. Werntz.** (*J. Amer. Chem. Soc.*, 1927, 49, 1584-1588.)—  
 Maize starch consists of a fatty-acid-bearing portion,  $\alpha$ -amylose, and a fat-free material,  $\beta$ -amylose, and amylose is apparently a fatty acid derivative of a carbohydrate complex. The Rask and Phelps alcohol-ammonia-water reagent removes only a small part of the combined fatty acids from raw starch and from maize  $\alpha$ -amylose, but raw starch may be freed of its combined fatty acids as follows. Two hundred grms. of dry starch are mixed with 600 c.c. of the Rask Phelps reagent (10 c.c. of 95 per cent. alcohol, 2 c.c. concentrated ammonium

hydroxide and 3 c.c. water for every 5 grms. of starch), boiled under a reflux condenser for 15 minutes, and, after settling, the supernatant liquid decanted, and the treatment repeated 8 times. The residue is washed with alcohol, and extracted for 8 hours with ether. The combined fatty acids then appear to be entirely removed. If extraneous nitrogenous and fatty material is first removed by treatment with alcoholic hydrochloric acid, prolonged and repeated reaction with the ammonium-alcohol reagent removes the fatty acids from the purified starch, but not from maize amylose itself.

D. G. H.

#### **Polarimetric Determination of Starch in Marzipan Substitutes.**

**A. Gronover and E. Wöhnlich.** (*Z. Unters. Lebensm.*, 1927, **53**, 252-261.)—Polarimetric determinations of starch have been made by the method of Baumann and Grossfeld (*ANALYST*, 1917, **42**, 218, 365) on the products of the various stages of the manufacture of marzipan from apricot kernels and sweet almonds. The factor for potato-starch of 1.77 (Ewers, *ANALYST*, 1916, **41**, 136) was employed. It is concluded that apricot kernels contain laevo-rotatory substances which are extracted by water and precipitated by hydrochloric acid, and consequently are also present when Ewer's method, in which the acid is employed directly, is used. The adoption of this method may also cause the production of dextro-rotatory substances as a result of hydrolysis of the pentosans, hexosans and pectins in the cell-substance itself; or, they may already be present in a form insoluble in water. Thus, after treatment with tannin, lead acetate, and sodium sulphate both dextro- and laevo- optically active substances remain in the insoluble portion. The Baumann-Grossfeld method, therefore, does not give quantitative results where the amounts of starch are small. These conclusions hold whether the product is roasted, or "bittered" or otherwise, and are unaffected by the presence of 23 to 24 per cent. of sugar.

J. G.

**Detection of Fruit Wine in Wine by means of a Microscopical Examination of the Turbidity.** **A. Widmer and O. E. Kalberer.** (*Z. Unters. Lebensm.*, 1927, **53**, 193-208.)—Microscopical examinations of the sediments and turbidities of genuine and suspected samples of Swiss red and white wines and musts have been carried out to detect adulteration with fruit wines (cider or perry). Detailed microscopical examinations of grapes, apples and pears showed that these fruits all contained starch, and experiments illustrated by photographs are described which enable the source of origin of the starch to be ascertained. As the result of a large number of counts in various fields of vision, the average number of starch granules in 100 fields of vision was determined, but no means of distinguishing between genuine wines and wines suspected on account of their tastes and analytical numbers, were obtained. Starch present in wine sediments and turbidities has its source in the original grapes, and the size and number of the granules present depend on the treatment received by the wine during the process of manufacture. A large number of round isolated starch granules may denote adulteration, if supported by other morphological evidence.

J. G.

**Spectroscopical Detection of Fruit Wine in Wine. O. E. Kalberer.** (*Z. Unters. Lebensm.*, 1927, 53, 208-221.)—Preliminary experiments on the determination, by Baly's method, of the absorption bands for lights of different wave lengths of red, white, and fruit (apple and pear) wines, showed that characteristic curves were obtained in each case when the logarithm of the thickness of the layer of liquid was plotted against the frequency of the light. It is preferable, however, to determine the extinction coefficient by Henri's method, that is, to compare the absorption spectra given by the sample for layers of liquid of various thicknesses and for various times of exposure, with the continuous spectra produced as a result of various times of exposure to a high frequency condensed spark discharge between iron electrodes. The logarithm of the extinction coefficient is then calculable from the times of exposure, the concentration, and the thickness of the liquid layer, and is plotted against the vibration number (reciprocal of the wave length) of the light used. Characteristic curves were again obtained, and the extinction coefficient of fruit wines was found to increase rapidly to a maximum at vibration number of 26,000 to 30,000, and then to fall to a sharp minimum at 38,000. The results confirmed those obtained by Baly's method. Examination of wines which contained known amounts of fruit wines as adulterants showed that the method may be made quantitative. Finings such as gelatin and tannin do not remove the absorbing substance, the nature of which is under investigation. Charcoal (eponite) however, produced a reduction in the extinction coefficient for Burgundy, cider and perry. J. G.

**Determination of Methanol in Presence of Ethyl Alcohol. F. S. Fortimer.** (*Ind. Eng. Chem.*, 1927, 19, 635-636.)—Examination of ternary mixtures of water, methanol, and ethyl alcohol at 20° C. by means of the Zeiss immersion refractometer, in order to test Leach and Lythgoe's refractometric method of analysing solutions containing both methyl and ethyl alcohols (*J. Amer. Chem. Soc.*, 1905, 27, 964), gives results which are much more regular for mixtures containing less than 40 per cent. of alcohol by weight than for stronger solutions. A ternary diagram is constructed which shows the refractivities of such mixtures; the lines of equal refraction, although nearly straight, are not quite parallel, and are not equally spaced. T. H. P.

**Comparison of the Sensitiveness of Various Tests for Methanol. J. O. Wright.** (*Ind. Eng. Chem.*, 1927, 19, 750-752.)—Oxidation with permanganate was found to be the best means of converting the methanol into formaldehyde, and Schiff's reagent is recommended for the detection of the aldehyde. The solution to be tested should contain 5 per cent. of alcohol, and the details of the method are as follows:—Three c.c. of the test solution are mixed in a test-tube with 1 c.c. of potassium permanganate solution (3 grms. of permanganate dissolved in 100 c.c. of water containing 15 c.c. of phosphoric acid); after ten minutes, 1 c.c. of oxalic acid solution (5 grms. dissolved in 100 c.c. of 1:1 sulphuric acid) is added, followed by 2 c.c. of Schiff's reagent. A violet coloration is produced if methanol is present, but with only a trace of methanol one hour may be

required for the development of the coloration. When glycerol or pectin is present the solution to be examined must be distilled and the test applied to the distillate. The test may be rendered quantitative by comparing the coloration obtained with those produced under the same conditions by mixtures of ethyl alcohol and methanol of known composition.

W. P. S.

**Iodine Value of a Commercial California Sardine Oil.** M. S. Dunn and B.<sup>5</sup>S. Hollombe. (*Ind. Eng. Chem.*, 1927, 19, 633-634.)—Determinations of the iodine value of five samples of the oil of the California sardine, *Sardinia caerulea*, by the Hübl and Hanus methods show that these two methods give concordant results, which furnish a reliable indication of the relative unsaturation of the oil. If the abnormally low results yielded by one of the five samples are discarded, the average value obtained is 177.8.

T. H. P.

**New Derivatives of Vanillin and some of their Reactions.** L. C. Raiford and G. C. Hilman. (*J. Amer. Chem. Soc.*, 1927, 49, 1571-1577.)—Condensation products of 5-bromovanillin studied included 5, 6-dibromovanillin characterised by a study of its derivatives 5, 6-dibromovanillidene-aniline, bis-5, 6-dibromovanillidene benzidine, etc. It was only found possible to isolate one of the stereoisomeric oximes of dibromovanillin; attempts to cause 5-bromovanillin to undergo the benzoin condensation were unsuccessful, and 5, 6-dibromo-3-methoxy-4-hydroxybenzo-nitrile was very resistant to hydrolysis with alkali.

D. G. H.

**The Detection of Carboic Acid in Commercial Cresol.** A. H. Ware. (*Pharm. J.*, 1927, 118, 775-776.)—It is shown that the B.P. test for carboic acid in "cresol" is useless, but that carboic acid, if present, can be detected by shaking it out from the mixed cresols with a limited quantity of fixed alkali, treating the solution of phenate thus obtained with dilute acid, shaking out the liberated carboic acid with ether, allowing the ether to evaporate and finally applying the new specific test for carboic acid recently described by the author (*ANALYST*, 1927, 335).

## Biochemical, etc.

**Relation of the Connective Tissue Content of Meat to its Protein Value in Nutrition.** H. H. Mitchell, J. R. Beadles and J. H. Kruger. (*J. Biol. Chem.*, 1927, 73, 767-774.)—The relation of the connective tissue content of meat to its toughness was established by Lehmann. (*Arch. Hyg.*, 1907, 63, 134), who showed that the toughness of meat depended largely upon its content of collagen and elastin fibres. It appeared probable that the proportion of collagen and elastin in meats would also be related to their protein values in nutrition, as indicated, for example, by the biological values of their digestible nitrogen; and thus, an increased connective tissue content would decrease the value of the nitrogen in the nutrition of maintenance and growth. With the use of the method of Mitchell, Zimmerman and Hamilton (*J. Biol. Chem.*, 1926-7, 71, 379) for the

determination of the collagen and elastin content of meat, an experiment was carried out to determine the biological value of the nitrogen of (a) a cut of meat of low connective tissue content, (b) a sample of connective tissue itself, and (c) a definite mixture of the two, such as would be found in the less desirable cuts of meat. The biological value of the nitrogen of pork tenderloin, containing a minimal amount of connective tissue, was found to be 79; that of pork cracklings, which consists largely of connective tissue, was 25. When the two materials were mixed in the proportion of 3 parts of tenderloin nitrogen to 1 part of cracklings nitrogen, the biological value of the tenderloin nitrogen was depressed to 72. Distinct indications of a supplementary relation between the nitrogenous compounds of muscle tissue and of connective tissue were noted. Reasons are given for believing that cuts of beef varying widely in their content of connective tissue would also vary widely in the biological values of their nitrogen, so that the less desirable cuts, containing large amounts of connective tissue, would be distinctly less valuable as sources of protein for maintenance and growth. This is not so true of pork, since different cuts of pork do not seem to vary greatly in their content of connective tissue.

P. H. P.

**Studies on Pentose Metabolism. II. Micro Method for the Determination of Pentoses and Pentosans. G. E. Youngburg.** (*J. Biol. Chem.*, 1927, 73, 599-606.)—The decomposition of pentoses or pentosans by means of hydrochloric acid has long been the most extensively used method for the transformation of these substances into furfural. It was thought desirable in the steam distillation procedure to replace the volatile hydrochloric acid in the distillation by some reagent which would not itself appear in the distillate, thus obtaining the furfural in a smaller volume, devoid of acidity, and therefore suitable for direct colour determination. All previously employed reagents and glycerol were tried, but all were eliminated except phosphoric acid. With phosphoric acid and steam pentoses may be determined in a micro way which is described. The furfural formed is determined by the following colorimetric method:—Five c.c. of the distillate are treated with 0.5 c.c. of aniline and 4 c.c. of glacial acetic acid, and the mixture made up to 10 c.c. and left for 15 minutes in the dark, after which the coloration is compared with that given by 5 c.c. of the furfural standard (0.05 mgrm. of furfural) under the same conditions. Phosphoric acid liberates furfural more rapidly than does hydrochloric acid from pentose material. In general, however, the yield of furfural is not greater than with hydrochloric acid. Numerous experiments were made to find conditions for maximum amounts of furfural to be produced. A table shows that only *d*-xylose is fully converted into furfural; *d*-ribose, *l*- and *d*-arabinose and *d*-lyxose follow in decreasing amounts of furfural yield. The furfural yields by this method from various carbohydrates and other substances are also given. From the data obtained it appears that only substances which contain a carbohydrate unit in the molecule, excepting methyl pentoses like rhamnose, and glycuronic acid may yield appreciable amounts of furfural. Body fluids may yield appreciable furfural from non-pentose

sources, such as from glycuronic acid, glycogen, dextrose and nucleic acid compounds. Under present circumstances, however, the method may be of value in following the course of the metabolism of substances which are predominately furfural-yielding.

P. H. P.

**Two Active Factors in the Vitamin B Complex.** W. D. Salmon. (*J. Biol. Chem.*, 1927, **73**, 483-497.)—Experiments are described which were carried out (1) to determine the relative antineuritic and growth-promoting values of the same samples of plant materials, and (2) to attempt a separation of extracts from those materials into fractions that might possess either the antineuritic or the growth-promoting action alone. Comparative tests on seed of the velvet bean and the soya bean, and on leaves of the velvet bean and of rape, have shown a higher antineuritic or beri-beri-preventing value for the seeds than for the leaves. The leaves are more potent than the seeds in their growth-promoting action. A fullers' earth fraction (activated solid) which prevented experimental beri-beri or polyneuritis of pigeons and rats, but which did not induce growth of rats has been prepared. Another fraction (the residue) which possessed extremely weak antineuritic or growth-promoting action when given alone as food, but marked growth-promoting action when added to the antineuritic fraction, has been obtained. The results have been interpreted as indicating further that the so-called vitamin B is a complex which contains two or more active substances, (1) a specific factor which prevents the occurrence of experimental beri-beri in pigeons and rats and (2) a factor which does not prevent the occurrence of beri-beri, and is not in itself capable of inducing growth, but which is a very potent promoter of growth when it is added to the factor which prevents beri-beri. It has been suggested that the term *vitamin B* be retained to designate the complex. It has also been suggested that the specific factor which prevents polyneuritis or experimental beri-beri be tentatively designated as *vitamin B-P*, or the beri-beri-preventing factor. A separate designation should not be proposed for the growth-promoting factor unless the results of further studies prove it to be non-identical with the factor *P-P*, or pellagra-preventing factor.

P. H. P.

**Vitamin C Content of Fresh and Canned Pear.** V. C. Craven and M. M. Kramer. (*J. Agric. Res.*, 1927, **34**, 385-391.)—The minimum protective dose of raw pear for guinea pigs was between 10 and 15 grms. daily, and taking orange juice as 100, its potency for vitamin C is estimated as 25. Canning by the cold pack method did not completely destroy the antiscorbutic factor, although no guinea pig survived the 90-day experimental period, but open kettle canning did destroy it. Storage had no effect on the vitamin C value of the pear.

D. G. H.

**Influence of Intense X-Ray and  $\gamma$ -Ray Radiations on Cholesterol.** M. C. Reinhard and K. W. Buchwald. (*J. Biol. Chem.*, 1927, **73**, 383-388.)—It was decided to follow the changes which X-rays and  $\gamma$ -rays would induce in certain organic compounds, and cholesterol was selected for the first study because

of its wide distribution in the body and its physiological activity there. The cholesterol was dissolved in chloroform or absolute alcohol to the extent of 0.4774 grm. in 25 c.c. After radiation the solutions were examined (1) chemically, (2) by means of the polariscope, and (3) in the ultra-violet spectroscope. The absorption spectra curves before and after X-ray radiation and  $\gamma$ -ray radiation are given and show similar changes. With increasing dosage the curves move toward the longer wave length, indicating increased absorption of ultra-violet light. Hess and Weinstock (*J. Biol. Chem.*, 1925, **64**, 193) increased the ability of cholesterol to absorb ultra-violet light by prolonged radiation with ultra-violet light. Chemical examination confirms the spectroscopic results that X-rays and  $\gamma$ -rays do cause a definite change in the molecule of cholesterol. One hour of X-ray radiation causes approximately the same change as 1000 millicurie hours of  $\gamma$ -rays. Curves show that after 26 hours with doses of X-rays and 25,000 millicurie hours with  $\gamma$ -rays the solutions are not approaching equilibrium. A chloroform solution of cholesterol (after 26 hours radiation with X-rays) was evaporated to dryness, and a brown wax-like substance resulted instead of the usual white crystals. The polariscope readings show a slight but progressive change for the shorter doses, but not for the longer periods of radiation. Therefore that part of the molecule which is responsible for the ultra-violet-absorption and for the chemical reaction is changed more than the part responsible for the optical activity.

P. H. P.

## Bacteriological.

**Pathogenic Bacteria and Mixed Enzymes of Milk.** C. Gorini. (*Compt. rend.*, 1927, **184**, 1355-1356.)—The author's observations on the behaviour of streptococci in the curdling of milk (*ANALYST*, 1926, **51**, 530) are extended to enterococci. These may behave as a simple (*i.e.* acidifying) enzyme or as a mixed (*i.e.* acid-proteolytic) enzyme according to whether they are derived from healthy or diseased sources, respectively. This is in agreement with the results obtained for *B. coli* derived from forage and grain, or from excreta. *B. pyogenes bovis* has also acid-proteolytic properties. An extension of the time of incubation led to the isolation of intermediate types which behaved either as mixed or simple enzymes, according to the temperature. The properties of mixed and simple enzymes are characteristic of parasites and saprophytes, respectively.

J. G.

**Identification of some of the Products formed by *Bacterium Pruni* in Milk.** S. L. Jodidi. (*J. Amer. Chem. Soc.*, 1927, **49**, 1556-1558.)—*Bacterium pruni*, causing a disease of plum and peach trees, gives rise to formation of crystals when grown in milk. On isolation and examination these were found to consist of needle crystals of tyrosine and globular aggregates, identified as leucine, whilst on heating the leucine-containing fraction with water, brown oily drops separated, regarded as a mixture of palmitic, myristic and stearic acids (undoubtedly produced from the milk fat) partly present as such, and partly in the form of a calcium salt.

D. G. H.



## Toxicological and Forensic.

**Sensitiveness of Some Reagent Papers towards Gaseous Hydrogen Phosphide.** M. Wilmet. (*Compt. rend.*, 1927, 184, 1456-1458.)—The sensitiveness towards phosphine of squares of filter-paper impregnated with the following solutions has been determined in stationary and moving atmospheres containing the gas:—Copper sulphate (10 per cent.), 0.1 *N* silver nitrate, potassium iodomercurate (10 per cent.). Winckler's alkaline iodomercurate, and mercuric chloride (5 per cent.). The exposed mercuric chloride paper may be sensitised and rendered specific to phosphine by immersion in a solution of potassium iodide (5 per cent.). It is then washed and dried. If it has been exposed to a small concentration of gas, a pale yellow or salmon colour results, whereas arsine produces a red-brown colour. The silver nitrate paper is the most sensitive, a brown-black colour being produced by a concentration of phosphine of  $10^{-6}$  after exposures of 2 and 3 minutes in a stationary and a moving atmosphere, respectively. The corresponding times for a sensitised mercuric chloride paper are 15 and 12 minutes, respectively. Above the concentration of 1/50,000, phosphine is detectable by its odour. The method is suggested for the determination of the gas in air. J. G.

**Hitherto Unsuspected Source of Arsenic.** R. E. Remington. (*J. Amer. Chem. Soc.*, 1927, 49, 1410-1416.)—American smoking and plug tobaccos were found to contain, by the micro-Marsh method, 6 to 30 parts per 1,000,000, or 0.05-0.27 grain of arsenic trioxide per lb., of which approximately half is evolved in the smoke of smoking tobaccos or is soluble in water in the case of the plug tobaccos. The proportions are in excess of those normally found in plants and animals. D. G. H.

**Sodium Selenite as a Cause of Poisoning.** F. Riechen. (*Z. Unters. Lebensm.*, 1927, 53, 264-266.)—The case is recorded of the presence of 1.15 grms. of selenium (corresponding with 2.5 grms. of sodium selenite) in 100 c.c. of coffee, and it is suggested that, on account of the physiological analogy between selenium and arsenic, this may be a source of poisoning. The selenium was determined according to the method of J. Meyer (*Z. anal. Chem.*, 1914, 53, 145). A suggested explanation of its presence is the sodium selenite used in the manufacture of the glass roof of the factory in which the coffee was prepared. J. G.

## Agricultural.

**Determination of Carbon and Nitrogen on the same Soil Sample.** B. E. Brown. (*Ind. Eng. Chem.*, 1927, 19, 629-630.)—Determination of carbon in soil by oxidising with a mixture of chromic and sulphuric acids, absorbing the carbon dioxide evolved in 4 per cent. sodium hydroxide solution, and subjecting the alkaline solution to double titration in presence of phenolphthalein and methyl

orange, gives results slightly lower than those obtained by the ignition method. Oxidation of the soil in the above way converts the nitrogen present into ammonium sulphate, so that the nitrogen may be determined by addition of sodium hydroxide to the residual liquid and distillation of the ammonia into standard acid. This procedure yields results agreeing well with those furnished by the Gunning method, but if manganese dioxide and sulphuric acid are used for the oxidation of the soil, somewhat higher figures are obtained on subsequent determination of the nitrogen in this way.

T. H. P.

**Determination of Organic Matter in Soils by means of Hydrogen Peroxide.** W. O. Robinson. (*J. Agric. Res.*, 1927, 32, 339-356.)—One gram. of soil or 0.2 gram. of peat is weighed into a tall 250 c.c. beaker containing 10 c.c. of water and 20 c.c. of 30 per cent. hydrogen peroxide, and covered. If the reaction is not too vigorous the beaker is heated on a steam bath. When bubbles cease to be evolved the hydrogen peroxide has disappeared. The liquid is filtered through a thick compact asbestos pad in a special Gooch crucible, the residue washed, and filtrate and washings evaporated, so that the ash of the soluble matter may be added to the weight of the residue. When 2 filtrations leave a muddy filtrate separate determinations of clay and soluble inorganic matter must be made. The insoluble matter on the pad is dried for 18 hours at 110° C. and weighed, and the moisture in the untreated soil determined. Cellulose, humus and lignite in soil are almost completely destroyed by hydrogen peroxide, whilst graphite is unattacked, and charcoal and coal partly decomposed. Determinations on soils and colloids containing from 0.42 to 95.85 per cent. of organic matter showed practically entire decomposition of organic matter in some cases, but not in others, the nature of the material remaining unattacked being somewhat uncertain. The method is regarded, on the whole, as accurate as the combustion method and more so in special cases, and an indication of the percentage of carbon in soil organic matter is obtained. Large proportions of calcium carbonate, manganese dioxide and chromium sesquioxide interfere with the method.

D. G. H.

**Sodium in Plants.** G. Bertrand and J. Perietzeanu. (*Bull. Soc. Chim.*, 1927, 41-42, 709-713.)—Sodium was determined in various parts of 35 plants, by first rapidly washing the fresh material in distilled water, weighing, drying, ashing, neutralising the aqueous ash solution by acetic acid, removing phosphoric acid by treatment with uranium acetate and centrifuging, and precipitating by Streng's reagent. The triple acetate crystals were collected in a Gooch crucible, washed and dried. All parts of the plants examined (including some previously reported as containing no sodium) were found to contain sodium, varying for the fresh material from 0.0006 per cent. (*Achillea mill. L.*) to 0.547 per cent. (*Zost. mar. L.*); and for the dried material from 0.0013 per cent. (chestnut fruit) to 3.507 (*Zost. mar. L.*), and in the ash from 0.016 per cent. (Japanese spindle tree leaves) to 16.78 per cent. (*Zost. mar. L.*).

D. G. H.

## Organic Analysis.

### Determination of Cyanates, with an Application to Potassium Cyanate.

**J. Leboucq.** (*J. Pharm. Chim.*, 1927, **119**, 531-538.)—The cyanate (0.2 to 0.5 gm.) is dissolved in a small quantity of water, and semicarbazide chlorhydrate added. After 24 hours the precipitated hydrazodicarbonamide is collected in a weighed Gooch crucible, washed with a saturated aqueous solution of the dicarbonamide, dried and weighed. The method was checked by determining the cyanate as ammonia and also by means of hypobromite. If a cyanide is present this must be eliminated, as it inhibits precipitation of the hydrazodicarbonamide. For this purpose excess of glucose is added, followed after 24 hours by semicarbazide hydrochloride and a drop of phthalein, and of acetic acid. After being shaken and left for 24 hours the precipitate may be collected as above. At least 1 per cent. of cyanate in cyanide may be definitely found by this method. It is essential that the final reaction should be acid.

D. G. H.

### Polarimetric Determination of Tartaric Acid. H. Besson.

(*J. Pharm. Chim.*, 1927, **119**, 539-544.)—To a known quantity of tartaric acid in solution are added 1 drop of phthalein, 5 drops of acetic acid and a volume of sodium oxalate and antimony (100 grms. of sodium binoxalate in 2 litres of water, and 25 grms. of antimony oxide boiled for 15 mins. and filtered) more than sufficient to convert all the tartaric acid into tartar emetic, followed by sodium hydroxide solution, drop by drop, until the precipitate first formed does not redissolve. After 5 minutes the exact quantity of acetic acid necessary to effect solution of the precipitate by the oxalic acid is added, the solution made up to known volume, and the polarimetric reading taken. In whatever form the tartaric acid was dissolved readings obtained were close to theory, and under the above conditions ranged from 302.44 to 303.74°.

D. G. H.

### Quantitative Determination of the Water-Insoluble, Higher, Saturated Fatty Acids in Fats and Fatty Acids. S. H. Bertram.

(*Chem. Weekblad*, 1927, **24**, 226-229.)—The methods of determination of saturated acids in oils and fats are reviewed critically. None gives satisfactory results, and the following is suggested for the determination of higher, water-insoluble fatty acids. The sample (5 grms.) is boiled for 1 hour under a reflux condenser with about 75 c.c. of an approximately 0.5 N alcoholic solution of potassium hydroxide, and the solution back-titrated with 0.5 N hydrochloric acid. The saponification value may then be calculated if a blank experiment is carried out. The unsaponifiable matter is next determined after the addition of 20 c.c. of the alcoholic potassium hydroxide and about 75 c.c. of water, by extraction with petroleum spirit (b.pt. 40-60° C.). The extract is washed, the solvent distilled off, and the residue weighed. The alcohol is then completely removed from the soap solution on the water-bath, and 5 c.c. of potassium hydroxide solution (50 Bé.) added. The liquid is well cooled, and 35 grms. of potassium permanganate in 750 c.c. of water added at a temperature below 25° C., so that a distinctly purple solution results. It is well shaken

from time to time, and, after oxidation is complete, the excess of potassium permanganate is removed by the addition of dilute solutions of sulphuric acid and sodium bisulphite. The solution is again extracted with petroleum spirit, washed with water, filtered and distilled, and the residue dissolved in ammonia. Ammonium chloride (10 per cent.), and magnesium sulphate (15 per cent.) are then added, and the resulting precipitate is warmed, filtered off in the cold, broken up in dilute sulphuric acid, and re-precipitated. Sulphuric acid is again added, the fatty acids finally extracted with petroleum spirit, and the extract washed, filtered, and distilled. The saturated fatty acid content of a number of oils and fats, and of oleic, elaidic, and stearic acids purified by different methods, have been determined. The greatest recorded error is  $-0.7$  per cent., but the average error is much lower.

J. G.

**Fractionation of Linseed Oil at 293° C.** H. D. Chataway. (*Ind. Eng. Chem.*, 1927, 19, 639-640.)—When linseed oil is heated for 2 hours at 110° C. in a current of carbon dioxide, then for 5 hours at 185° C. under about 15 mm. pressure, and finally for 7 hours over a naked flame at 293° ( $\pm 4^\circ$ ) C., at either atmospheric or 15 mm. pressure (*cf.* Long, *Ind. Eng. Chem.*, 1927, 19, 62), as much as 56 per cent. of a fraction insoluble in acetone may be formed. These fractions show high molecular weights and are essentially colloidal; they are also viscous and set to a solid mass on prolonged heating at 80° C., and it seems probable that the viscosity and setting power of the treated oil are due to such fractions. If the raw oil is heated at 293° C., without previous heating at 185° C. *in vacuo*, no insoluble fraction is formed, although the viscosity of the oil increases normally.

T. H. P.

**Oil from Port Orford Cedar Wood.** F. H. Thurber and L. J. Roll. (*Ind. Eng. Chem.*, 1927, 19, 739-742.)—The light brown oil obtained from Port Orford cedar wood (*Chamaecyparis lawsoniana Parlatores*) examined had the following characteristics:—Sp. gr. at 20° C., 0.8913;  $n_D^{20}$ , 1.4760 [ $\alpha_D^{20}$ , +46.68; acid value, 0.19; ester value, 19.3; ester value after acetylation, 88.3. The ester values before and after acetylation were equivalent to 5.1 per cent. of bornyl acetate and 20.5 per cent. of free borneol. On distillation, the following fractions were obtained, each fraction being named from the principal constituent which it contained:—*d*- $\alpha$ -pinene, 45.7; *d*-limonene, 3.2; *d*-borneol, 26.0; *d*-cadinene, 21.0; *l*-cadinol, 3.9 per cent.

W. P. S.

**Action of Sulphur Monochloride on Petroleum Hydrocarbons.** E. Lorand. (*Ind. Eng. Chem.*, 1927, 19, 733-735.)—Preliminary experiments showed that the action of sulphur monochloride on petroleum hydrocarbons is a general reaction for unsaturated hydrocarbons; it consists probably of chlorination and subsequent condensation or polymerisation. Saturated hydrocarbons are also attacked, but more slowly, and it is suggested that by controlling the reaction, a means might be found for determining the degree of unsaturation of petroleum hydrocarbons.

W. P. S.

**Nature of Matured Rubber. II. G. Bruni and T. G. Levi.** (*Giorn. Chim. Ind. Appl.*, 1927, 9, 161-164.)—The aqueous fraction obtained by shaking the acetone extract of matured slab rubber with a mixture of water and ether comprises: (1) About 10 per cent. of a mixture of an  $\alpha$ -aminovaleric acid with two  $\alpha$ -aminocaproic acids, one giving a readily soluble, and the other a sparingly soluble copper salt; these amino-acids, which do not influence vulcanisation, are obtainable also from the acetone extract of smoked sheet. (2) More than 30 per cent. of potassium phenylacetate, which is an energetic accelerator of vulcanisation; vulcanisation is promoted greatly by potassium, and slightly by sodium salts of fatty and fatty-aromatic acids, whereas the potassium salts of aromatic acids have but little, and the corresponding sodium salts virtually no effect. (3) About 20 per cent. of a mixture of tetra- and penta-methylenediamines, this acting as a vigorous accelerator of vulcanisation. The ethereal fraction contains phytosterol, which is without influence on vulcanisation. T. H. P.

**Preparation of Phosgene from Chloropicrin. S. Secareano.** (*Bull. Soc. Chim.*, 1927, 41-42, 630-631.)—Chloropicrin is rapidly and entirely decomposed at 100° C. by fuming sulphuric acid (20 per cent. anhydrous), producing 1 molecule of phosgene and one of nitrosyl chloride. The phosgene may be collected in a freezing mixture. Besides pyrosulphuric chloride, nitrosyl sulphate remains in the flask, and gives with diphenylamine an intense blue colour. Chloropicrin may thus be detected, and if 2-3 c.c. of concentrated sulphuric acid containing a little diphenylamine in solution are heated to about 130° C. and the air from a flask containing a little chloropicrin introduced into the reagent by a tube, the blue colour forms almost instantaneously. D. G. H.

**Determination of Nitrogen in Leather. L. Balderston.** (*J. Amer. Leather Chem. Assoc.*, 1927, 22, 261.)—The Analysis Committee of the American Leather Chemists' Association for the determination of nitrogen has been studying the effect on the accuracy of the determination of (1) absorbing the distillate from the Kjeldahl process in saturated boric acid; (2) using indicators other than methyl orange; (3) varying the weight of leather taken. The Committee finds the boric acid method with brom-phenol blue as indicator titrated with semi-normal acid to be the most convenient and satisfactory. The amount of leather recommended for each analysis is 1.4 grms. The use of larger amounts than 1.4 or 1.5 grms. tends to produce undue frothing at the beginning of the digestion. Results are only reliable to one decimal place (3 significant figures). R. F. I.

**Reactions of Dyestuffs with Nitrous Acid. J. V. Dubsky and A. Okáč.** (*Rec. Trav. Chim. Pays Bas*, 1927, 46, 296.)—The authors have carried out experiments on some 600 dyestuffs with the object of observing the colour changes which take place on diazotising and condensing with phenol,  $\alpha$ -naphthol and  $\alpha$ -naphthylamine. From 10 to 50 mgrms. of the dyestuff were dissolved in 100 c.c. of water and diluted till the solution was transparent. To 2 c.c. of a solution of potassium nitrite (containing the equivalent of from 0.01 mgrm. to 10 mgrms.

of nitrous acid, *i.e.*  $10^{-8}$  to  $10^{-5}$ ), 1 to 5 drops of the dye solution were added, and the mixture shaken with 1 c.c. of *N* hydrochloric acid. After 10 minutes a few crystals of the "coupling reagent" were added, and the solution made alkaline with ammonia or sodium hydroxide. A table shows the results obtained with 16 various dyestuffs of different origin, from which the following examples are taken :—

Dyestuff.	Colour of solution.	HNO <sub>2</sub> .	Condensing Agent.		
			Phenol.	$\alpha$ -Naphthol.	$\alpha$ -Naphthylamine.
Benzidine	colourless	yellow 6	yellow	red 7	violet 7
Phosphine	yellow	yellow	orange 5	red 7	red 7
Primuline	"	"	" 7	" 7	" 6
Amidoazobenzene	"	"	" 6	" 7	" 6
Rhodamine	red	colourless 5	blue 6		blue 7

The figures denote the sensitiveness of the reaction, *e.g.* 6=nitrous acid of concentration  $10^{-6}$ .

R. F. I.

## Inorganic Analysis.

**Some Sources of Error in the Colorimetric Determination of  $P_H$  Values.** J. W. Schlegel and A. H. Stueber. (*Ind. Eng. Chem.*, 1927, **19**, 631-633.)—The comparison tubes supplied for the colorimetric determination of  $P_H$  values are often incorrectly marked; thus, in one batch of such tubes the supposed 10 c.c. marks corresponded with 9.0, 9.2, 9.4, 9.5, 10.0, 10.5, and 11.8 c.c. respectively. The preliminary dilution of dark liquids with indiscriminate proportions of water, commonly practised in sugar factories, may lead to pronounced errors, probably owing to alterations in the degree of dissociation of the complex mixture of salts and other substances present. When used for virtually unbuffered solutions, tubes which have been dried in the oven almost invariably give high results, unless they are first rinsed out with the solutions. Mixing of the dye and sugar solution in a tube closed by the finger leads to contamination by the acid secretions of the skin; this may be avoided either by pouring the liquid several times from one tube to another or by the use of pyrex tubes with ground stoppers. The wax used for coating storage bottles for buffer and other solutions should be free from acid, but for such storage it is better to use pyrex bottles, in which bromothymol blue solution remains unchanged for prolonged periods, unless the bottles are frequently opened. When weakly buffered solutions are to be tested, it is recommended that the dye solution be either kept in a pyrex burette fitted with a soda-lime tube or syphoned directly from a pyrex stock bottle protected by a soda-lime tube. Comparison with the standard tubes should be made promptly, as the colour begins to fade at once, especially with dilute, slightly buffered solutions.

With such solutions it is important that acid dye solutions, *e.g.* those of bromothymol blue, should be neutralised with the proper quantities of sodium hydroxide. Satisfactory results are obtained by the use of water of  $P_H$  7.0 prepared by Dawson's method (*J. Phys. Chem.*, 1925, **29**, 551), which consists in boiling

off one-third of the volume of a good distilled water and storing the remainder out of contact with air in insoluble glass containers. The bromothymol blue is dissolved in such water to which successive small amounts of dilute sodium hydroxide solution are added until the liquid, tested against the water of  $P_H$  7.0, gives a colour corresponding with that given by the same indicator solution tested against a buffer solution of  $P_H$  exactly 7.0.

T. H. P.

**Absence of Stratification and Rapidity of Mixing of Carbon Dioxide in Air Samples.** T. M. Carpenter and E. L. Fox. (*J. Biol. Chem.*, 1927, **73**, 379-381.)—A problem in metabolism studies which are dependent upon the analysis of gas samples is the question of adequate mixture of the sample and the possibility of the carbon dioxide settling in the lower portion of the sampling vessel, if the sample is allowed to stand for hours or days before analysis. It is believed that differences in the specific gravity of gases may cause stratification, and that different rates of diffusion may cause inadequacy of mixture. A sampling tube of 1040 c.c. capacity, with stopcocks at the ends having outlets at the end of the stopper, was filled with dry air to which a small amount of carbon dioxide was added. The sample was thoroughly mixed, and the gas was analysed immediately and on successive days, until all the sample was used. There was no indication of stratification on standing. The rapidity of mixture of carbon dioxide with air was also determined. The same sampler was filled with room air, and pure carbon dioxide was introduced into the lower stop-cock. A slight pressure was put on the gas by the careful admission of mercury at the lower end, and analyses were made on the sample until constant composition was reached. The results are tabulated. In the first two series the samples were drawn into the gas analysis apparatus by the washing method, and in the second two series by the displacement method. In the first two, complete mixture was reached in 36 and 37 minutes respectively, and, in the second two, in 1 hour and 20 minutes and 1 hour and 25 minutes, respectively. Therefore the diffusion was rapid and complete even under extreme conditions.

P. H. P.

**New Highly Sensitive Microchemical Reactions for Cadmium Salts.** A. Martini. (*Anal. Asoc. Quím. Argentina*, 1927, **15**, 52-56.)—When a drop of from 1 to 0.05 per cent. cadmium chloride solution is spread on a microscope slide and one edge of it is touched, by means of a gold pen, with a drop of caesium chloride solution and then with a drop of saturated sodium phosphate solution, a white precipitate is formed. If the other side of the drop is touched with a drop of saturated sodium bromide solution and then with a drop of concentrated brucine acetate solution, another white precipitate forms. If now the cover-glass is applied and the precipitates examined under the microscope, the first is seen to consist of tetrahedra of caesium and cadmium phosphate, and the second of characteristic radiating masses of pointed crystals of cadmium brucine bromide. The latter are obtained also when the drop of cadmium chloride solution is mixed with a drop of a saturated solution of a salt of any of the common metals; the

mixed drop may then be treated as well with a microchemical reagent for the added metal. In all cases this reagent for cadmium proves to be specific and sensitive. Similarly, characteristic microscopic crystals of cadmium quinine bromide are obtained on adding a small quantity of saturated sodium bromide solution and then a small drop of a concentrated acetic acid solution of quinine sulphate to a drop of 0.1 or 0.05 per cent. cadmium chloride solution. T. H. P.

**Determination of Copper.** G. Spacu and J. Dick. (*Z. anal. Chem.*, 1927, 71, 185-189.)—The precipitation as  $\text{CuPy}_2(\text{CSN})_2$  (ANALYST, 1925, 50, 580) is described, but the precipitate, instead of being ignited to constant weight, is weighed in a tared porous porcelain crucible after having been washed in succession with solutions of precipitant in water, alcohol, and ether, and dried *in vacuo* or at 45° C. The procedure provides a separation of copper from the alkalis, alkaline earths, and mercury, but not from nickel, cobalt, manganese, zinc, cadmium, "etc." The presence of ammonium salts is immaterial. (Cf. ANALYST, 1927, 430.) W. R. S.

**Determination of Arsenic Pentoxide as Magnesium Ammonium Arsenate.** W. M. McNabb. (*J. Amer. Chem. Soc.*, 1927, 49, 1451-1453.)—Application of the method of Brookman and Schmitz (*Amer. J. Chem. Soc.*, 1927, 49, 891) to the determination of arsenic pentoxide as magnesium ammonium arsenate indicates that no advantage in accuracy is to be gained, although the fact that precipitation is complete in half an hour, and that ignition of the final product to constant weight should be made at 500-600° C., simplifies the process. The average error was -0.02 per cent. D. G. H.

**Determination of small Quantities of Zinc in Aluminium.** W. Böhm. (*Z. anal. Chem.*, 1927, 71, 243-246.)—It is pointed out that the insoluble residue from the solution of the metal in caustic soda is not free from zinc. The residue is dissolved in hydrochloric acid and bromine, the copper precipitated by hydrogen sulphide, and the filtrate neutralised and acidified with formic acid; the zinc is precipitated as sulphide, which is converted into oxide by gentle ignition. The main sodium hydroxide filtrate is precipitated with sodium sulphide, the precipitate dissolved in hydrochloric acid, and the zinc precipitated with hydrogen sulphide as before, after treatment with ammonia and formic acid. W. R. S.

**Determination of Zinc by Means of Oxyquinoline.** R. Berg. (*Z. anal. Chem.*, 1927, 71, 171-185. (Cf. ANALYST, 1927, 431, and next abstract.)—Zinc is precipitated from acid acetate, ammoniacal, or alkaline tartrate solutions as greenish-yellow, crystalline  $\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ . The sensitiveness is 1:1,000,000 in acetic, 1:277,000 in ammoniacal, and 1:140,000 in alkaline tartrate solution. Dried at 100° C., the precipitate retains  $1\frac{1}{2}\text{H}_2\text{O}$  (17.18 per cent. Zn); it becomes anhydrous at 120° to 130° C. (18.49 per cent. Zn). Precipitation from acetic solution is the most suitable procedure: it allows a separation from magnesium and the other alkaline earths to be made, but not from copper or cadmium. The



neutral solution (100 c.c.) is treated with a few drops of acetic acid and 3 to 5 grms. of sodium or ammonium acetate; it is warmed to 60° C., then precipitated with a freshly prepared, 2 per cent. alcoholic solution of the reagent while the temperature is raised to incipient boiling. Complete precipitation is indicated by the yellow colour of the solution (oxyquinoline acetate). The precipitate is collected in a porous glass crucible and washed with hot water. For the gravimetric determination, it is dried at 100° to 105° or 120° to 130° C., the respective factors given above being used. Drying at the lower temperature produces slightly high, at the higher temperature, slightly low results. Titration is most convenient, quick, and accurate: the washed precipitate is dissolved in 2*N* hydrochloric acid, and titrated with 0.2 to 0.05 *N* bromate-bromide solution in presence of indigocarmine; when excess of bromine is indicated, potassium iodide is added and the liberated iodine titrated with thiosulphate. 1 c.c. 0.1 *N* Br = 0.000817 gm. Zn. An acetic acid concentration of about 0.5 per cent. suffices to hold 0.1 to 0.15 gm. of magnesium in solution, hence the present method answers well for zinc-magnesium alloys; the magnesium in the filtrate is precipitated by oxyquinoline in ammoniacal solution. The precipitation from alkaline tartrate solution is carried out in presence of 3 to 5 grms. of sodium tartrate and a maximum of 20 c.c. of 2 *N* sodium hydroxide per 100 c.c. In this manner zinc may be precipitated in presence of ferric iron, aluminium, and chromium; if cobalt and nickel are present, the zinc precipitate should be re-dissolved in a little warm 10 per cent. hydrochloric acid and the precipitation repeated. The metals of the hydrogen sulphide group—mercury excepted—do not interfere with the precipitation of zinc from alkaline tartrate solution, though the presence of substantial amounts of lead and bismuth necessitates double precipitation. For the separation from mercury, the solution is treated with a few c.c. of 0.2 *N* cyanide solution, acidified with tartaric acid (3 grms.), and neutralised with sodium hydroxide against phenolphthaleine; an excess of 2 *N* sodium hydroxide (15 c.c.) is added to the solution measuring 100 c.c. Oxyquinoline is added in the cold; the solution is warmed to 60° C. and cooled, the precipitate collected, washed, and dissolved and titrated as above.

W. R. S.

**Acidimetric Determination of Magnesium Zinc, Aluminium, and Copper in Presence of Oxyquinoline.** F. L. Hahn and E. Hartleb. (*Z. anal. Chem.*, 1927, 71, 225–235. Cf. preceding abstract.)—The precipitation of certain metals as oxyquinoline complexes permits the volumetric determination by alkali of the acid combined with the metal. The presence of oxyquinoline does not interfere with the titration of strong acids by alkali, but the metallic precipitate adsorbs the indicator. The mode of working described below overcomes this difficulty, and the method gives results agreeing within one drop of 0.1 *N* solution. Phenol red is especially serviceable; its decided end-point can be observed in presence of large amounts of yellow precipitate; if the solution contains nitrate, naphtholphthalein will be found preferable. If the liquid is shaken with carbon tetrachloride during the titration, the excess of reagent and the precipitate are removed from the solution, which clears almost completely. If large amounts of

metal are to be titrated, the precipitate, before the final neutralisation, may be left to settle, and the titration completed on an aliquot part of the almost clear liquor. Large amounts of barium chloride do not interfere, hence the filtrate from a barium carbonate emulsion treatment can be titrated direct for zinc or magnesium. Calcium, on the other hand, must be removed, though the oxalate precipitate need not be filtered off: the solution is treated with oxalic acid, then neutralised with sodium hydroxide (phenolphthalein) on the water-bath, the final adjustment being made with 0.1 *N* alkali. *Magnesium*: the acid solution is neutralised against phenol red, treated with a slight excess of 5 per cent. alcoholic oxyquinoline solution, and titrated hot with sodium hydroxide to red. If all the magnesium has been precipitated, further addition of the reagent at this point does not alter the colour to yellow. The liquid is at once titrated to yellow with 0.1 *N* acid, an excess of 2 to 3 c.c. of which is then added. After warming for 10 to 15 minutes and cooling, the final titration to red with 0.1 *N* alkali is made. *Zinc*: the free acid is neutralised against phenol red. Oxyquinoline is added, the liquid boiled gently for 5 to 10 minutes, and titrated hot to red. A small excess of 0.1 *N* acid is added, and the final adjustment with 0.1 *N* alkali made as for magnesium. *Aluminium*: the free acid is determined in a separate portion: 10 c.c. are treated with 70 c.c. of cold saturated sodium oxalate solution and titrated against phenolphthalein (the oxalate solution should previously be neutralised against the same indicator). The free, *plus* the combined acid is determined as the combined acid in the case of magnesium, and the free acidity deducted from this result. *Copper*: the free acid is neutralised against methyl orange. The solution, containing excess of reagent, is boiled gently for 5 to 10 minutes, the precipitate changing from a flocculent to a finely crystalline condition. After addition of phenol red, the liquid is titrated to red with 0.1 *N* alkali, to yellow with 1 to 2 c.c. excess of 0.1 *N* acid, boiled for a short time, cooled, and adjusted finally with 0.1 *N* alkali.

W. R. S.

#### **Manganese Interference in the *o*-Tolidine Test for Available Chlorine.**

**E. S. Hopkins.** (*Ind. Eng. Chem.*, 1927, 19, 744-756.)—It is shown that manganese salts yield a yellow coloration with *o*-tolidine reagent similar to that given by chlorine. Even manganese sulphate, after it has been converted into the hydroxide by the addition of an alkali and then dissolved in an acid, will give a coloration owing to the absorption of oxygen by the hydroxide.

W. P. S.

**Determination of Ferrous Iron in Silicates.** **L. A. Sarver.** (*J. Amer. Chem. Soc.*, 1927, 49, 1472-1477.)—When using diphenylamine as indicator for the titration of ferrous iron by potassium dichromate it is important to keep the titration volume small; to add only a few drops of dichromate solution after the first trace of violet has been observed, and to make the final adjustment of volumes quite deliberately. With diphenylamine the presence of hydrofluoric acid renders the iron very sensitive to oxidation. Dichromate slowly oxidises hydrofluoric acid at high temperatures. For the analysis of a silicate rock 0.5 grm. of coarse

powder is moistened with water, treated with 10 c.c. of 12 *N* hydrochloric acid or 18 *N* sulphuric acid, and a special bakelite cover provided with a tube for introduction of carbon dioxide and a funnel for adding hydrofluoric acid and for escape of vapours is fitted to the platinum crucible, and carbon dioxide is passed through the flask for at least 10 minutes, while the mixture is heated to boiling, after which the gas is stopped and about 7 c.c. of 40 per cent. hydrofluoric acid added, and the mixture boiled for 10 to 15 minutes. When decomposition is complete the gas stream is restarted, and, as soon as the liquid is cool enough, an excess of dichromate added through the funnel, the contents of the crucible poured on to solid boric acid in a ceresin-lined porcelain basin, and at once titrated with standard ferrous solution, with diphenylamine as indicator. Results agreed well and were somewhat higher than those obtained with an ordinary crucible. D. G. H.

## Physical Methods, Apparatus, etc.

**Applications of a Mobilometer.** H. A. Gardner and A. W. Van Heuckeroth. (*Ind. Eng. Chem.*, 1927, 19, 724-726.)—The apparatus, which is a kind of falling disc viscometer, consists of a brass cylinder, 3·89 cm. in diameter and 22·85 cm. in length, fitted with a movable bottom which screws into a base-plate. A plunger rod, 0·635 cm. in diameter and 50·8 cm. in length, passes through a bearing centrally down the cylinder, and to the bottom of this rod may be fixed discs of slightly smaller diameter than the cylinder. The discs may be perforated or not, for use with liquids of different viscosity, and weights may be placed on a platform at the top of the rod, so that a reasonable time of fall of the rod is attained. The cylinder is filled with the liquid until the level reaches a mark 2 cm. from the top, and the time is noted for the plunger to fall from the surface of the liquid to the bottom of the cylinder; a small pointed rod is fitted on the under side of the discs, and when this touches the bottom of the cylinder a click is heard. The apparatus may be used for comparing the viscosities or consistence of such liquids as paints, mineral oils, tars, soap solutions, etc. W. P. S.

**Testing of Dyestuffs for Fastness to Washing.** S. R. Trotman. (*J. Soc. Dyers and Colourists*, 1927, 43, 192.)—Fastness of dyes may be numerically expressed by drying under standard conditions, testing a weighed portion of the dyed sample by washing under standard conditions, squeezing back the soap liquor into the bath, washing with hot distilled water which is then added to the bath liquor, cooling the liquor and washings, making up to definite volume, and matching a similar volume of soap solution containing the same weight of soap by adding a standard solution of dye. D. G. H.

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## Reviews.

THE CHEMISTS' YEAR BOOK, 1927. Twelfth Edition. Edited by F. W. ATACK, D.Sc. Pp. 1180 and Index. Manchester: Sherratt & Hughes. Price 21s.

The fact that the "Chemists' Year Book" has now reached its twelfth edition is a strong indication of its continued popularity. The advance of knowledge renders necessary not only the revision of existing data and methods, but also the inclusion of fresh material, and though the new issue retains the size and general form of its predecessor there are a number of changes. The section on "Trade Names of Drugs" has been incorporated in the section on "Pharmaceutical Names of Synthetic Compounds." The latter has been completely revised, and the same applies to the sections on "Analysis of Portland Cement," "Agricultural Chemistry," and "Dairy Products."

It is unfortunate that the section on  $P_H$  values has been postponed until the next edition, as it is long overdue. In this connection a plea might be made for the inclusion in some of the other sections of information on the influence of the hydrogen ion concentration. This applies particularly to the sections on Electrochemical Analysis, Brewing Materials, Wort and Beer.

In a book of this type general criticism will necessarily be directed principally towards those sections of interest to a particular individual. In the chapters which deal with the analyses of Coal and Liquid Fuels reference should have been made to the standardised methods published by the Fuel Research Board and the Institution of Petroleum Technologists, respectively, in the same way as has been done in the case of the analysis of Cement and Malts,

In the sections on the analysis of Brewing and allied materials the Lintner method for the determination of starch and also "formol" titration should have been described. The colour value of sugars which is not mentioned is also considered to be of importance when these are required for brewing purposes. A reference is made in the case of the determination of milk sugar to Lane and Eynon's volumetric method, in which the methylene blue indicator is employed. This might well have been described in full and extended to replace the use of Ling and Rendle's external indicator in the determination of sugars by the Fehling-Soxhlet method, and also for Lintner's method for the determination of the diastatic activity of malt. It should be noted that dianol-green possesses certain advantages which render it preferable to either indicator in the latter case. In the analysis of hops a number of most valuable biological methods have been evolved since the date of the most recent reference quoted (1913), and the Institute of Brewing has in recent years published comparative analyses made by the different methods.

No mention of nitrites is made in the section on the detection of preservatives in milk, and the method recommended for the determination of boric acid in butter is not the most reliable, particularly in view of the new Public Health Regulations.

The directions for the determination of the unsaponifiable matter in oils and fats also, are inadequate and likely to give low results in many cases. Titanium is not mentioned in the section on paints and pigments.

A few misprints have been noted. The name Beckmann is mis-spelt on p. 654, and a word is omitted on p. 928. On p. 528 the deep blue copper-ammonium complex is referred to as an ion and represented as a molecule, whilst some of the formulae of organic compounds and many of the formula-weights are incorrect.

The importance of subjects such as enzymes and vitamins surely warrants their inclusion in some future edition. Indicators also are now so widely used that some collected information regarding them would be welcomed. A slight objection might also be raised to the fact that the correction of barometer readings and tables of specific gravities and densities are separated by almost the whole length of the book from the conversion of barometer readings and the hydrometric tables.

Periodical publications of this type which benefit (one hopes) from an annual stream of criticism should tend towards perfection along an asymptotic path. The Editor in fact invites constructive criticism for the improvement of future editions. It should be stated however, in conclusion, that the criticisms are few in number and relatively unimportant compared with the great wealth of information contained in the book, and they in no way detract from its established value to the chemist.

JULIUS GRANT.

DIE CHEMIE DER NAHRUNGS- UND GENUSSMITTEL. FRANZ FUHRMANN. Pp. 610.  
Berlin: Urban and Schwarzenberg. 1927. Price

This is a valuable work on foods written primarily from a physiological point of view. It is addressed both to the chemist and the physician, and therefore first thoroughly describes the anatomical and physiological mechanism of the assimilation of food. Next follows a consideration of the chemistry of the enzymes concerned in digestion, and of the elements and compounds found in different parts of the body and in foodstuffs. These subjects are clearly and accurately set out (so far as the reviewer is able to check them), and with the chapters on energy values and vitamins, form an invaluable preliminary to the detailed study of foods, which commences in Part II, on p. 171. The treatment of the subject is well balanced and can be commended to the notice of all chemists who contemplate the food and drugs branch of our profession.

The larger part of the book gives detailed accounts of the various foodstuffs; their origin, preparation, properties, food-values and composition are described. Analytical matters are only mentioned quite briefly, so that, while useful tables of composition appear, the author is not concerned with the technique of food analysis. A noticeable feature of these chapters is their comprehensiveness; no other book with which the writer is familiar gives quite so good an account of the origin and preparation of foodstuffs, except, perhaps, the encyclopaedic "König." No important—and few unimportant—foods or components are left undescribed. The outlines of the manufacturing processes involved in the preparation of each foodstuff form a particularly useful feature.

There are a few points of criticism to be mentioned. There is an unfortunate absence of references to original works, or to the authorities on a particular subject; the addition of such in a future edition would be useful. Where names are mentioned they are nearly always German; indeed, one wonders how nine pages can be written on vitamins without referring to Sir Frederick Hopkins or to any English or American worker. A subject on which more information would be welcome is that of preservatives; one looks in vain for any discussion of the physiology or therapeutics of these substances; methods of preservation are mentioned, but not treated critically. Lastly, a work of this size and merit is worthy of a cloth binding rather than of paper covers.

The book will form a valuable addition to the library of all food chemists.

H. E. Cox.

THE MICROBIOLOGY OF CELLULOSE, HEMICELLULOSES, PECTIN AND GUMS. By A. C. THAYSEN and H. J. BUNKER. First Edition. Pp. viii. +363, with 23 illustrations. London: Humphrey Milford. 1927. Price 25s. net.

This work has been written primarily for the research worker in microbiology, and is intended as a comprehensive guide to the literature of the subject which in recent years has become of steadily increasing importance in connection with the decay of vegetable products.

The book is divided into four parts, the first being devoted to the occurrence and properties of cellulose, hydrocelluloses, pectins, and gums, whilst part 2 deals with the classification, nomenclature and cultural characteristics of the various types of organisms, including the Schizomycetes, Actinomycetes and Eumycetes, causing decay of these substances. Part 3 provides details of the physical and chemical processes occurring during the microbiological decomposition of silage, peat, wood, textile fabrics, etc., and in Part 4 the industrial applications of these reactions are described, although frequent references to this part of the subject occur throughout the volume.

The text is by no means a disjointed collection of data and facts, for the wide experience of the authors has enabled them to produce a readable resumé of most of the literature published during the last ninety years. This has been woven into a harmonious whole including judicious and critical discussions of the results obtained by various investigators and, with unusual honesty, the earlier work of the authors themselves, whilst in addition many useful practical details are given. That the work was an onerous one is evident from the comprehensive range of the subject matter and the meticulous care taken to ensure accuracy.

Perusal of this work illustrates the rapidly increasing interest taken in the subject during the last few years, but one is also impressed by the enormous field awaiting investigation in several directions, and workers wishing to devote their energies to some interesting biological research likely to prove of value to the community at large will find many helpful suggestions scattered throughout the volume.

Much care has been expended upon the proof reading, for one trifling typographic error only has been met with, whilst the index and the extensive bibliographies appended to nearly every chapter are complete and accurate, although reference to the work of Baxter and of Mangin and Patouillard appears to be omitted.

The book is well bound, the type clear and the photomicrographs and other illustrations are excellent, but the value of the former would have been enhanced had the magnification been given in every case.

The volume as a whole is of a high order of merit and will prove invaluable to many workers, for it is seldom that such a wealth of information on microbiology is contained within such a relatively small compass. T. J. WARD.

THE METALLURGIST'S MANUAL. By T. G. BAMFORD, M.Sc., and HAROLD HARRIS, M.Sc. Pp. x. +246. London: Chapman & Hall. Price 15s. net.

In the preface the authors submit that their book is intended for metallurgists, students and engineers, and others interested in metals.

"The book provides a sound method for carrying out almost every analysis or assay commonly met with in mining and metallurgy—how to conduct examinations of fuels refractories—calculate furnace changes—explains methods of measuring high temperatures, and finally contains the essential information respecting the metallography properties and uses of the chief industrial alloys."

This is attempted in the space of some 240 pages. The methods given cover the assay of precious metals, the non-ferrous metals and alloys, iron, manganese, steel and the examination of fuels; hence, whilst the programme is comprehensive, in presenting this whole series of methods there is, as a consequence, a paucity of essential details, so that the descriptions of working methods read as though they had been put together by a process of transference from a collection of working notes.

Occasionally one encounters an expression of personal opinion which, however, is not always supported by any weight of evidence; as an example, under the heading "Manganese in Steel," after describing the Bismuthate and Volhard methods, the authors give the equally well-known Gravimetric Acetate Separation method, using 5 grms. of sample, fractionating a half. Here they make the statement that, when properly carried out, the gravimetric process gives greater accuracy than the volumetric process. This is debatable and should certainly be supported by evidence, if notice of it is to be taken.

Under the description of the Molybdate Method for lead in ores and furnace products, the reader is told to deduct 1.5 per cent. for selling assay. Why lead has this singular distinction is not stated.

In the case of iron ores, one would suggest that moisture be determined on a greater quantity than 1 grm. particularly where an invoice is to be based on an analysis of the material. Under the heading of heating value of fuels, a considerable amount of information is supplied in a very small space. Definitions

are given of the various heat units in current use, with factors for their inter-conversion. The law of constant heat summation is illustrated by the combustion of carbon monoxide, but no mention is made of the fundamental energy law underlying the phenomena.

"Calorific intensity" and "Evaporative Power" are discussed in some detail, and the methods in common use for the analysis of coal are described. Thomson's calorimeter and the methods for its use are fully described, but the bomb calorimeter is merely mentioned, in passing, with the remark that "in order to obtain the calorific power at constant volume, which gives the highest possible results, a bomb calorimeter is employed."

The section on Metallography is, however, distinctly informative, and the illustrations chosen are admirable. It is rather surprising to find that the authors apparently continue to subscribe to the  $\beta$  iron theory.

As a whole, the book contains a mass of well-condensed information on different subjects not usually collected together in one volume. In this lies its strongest feature, and its utility to those already conversant with the subjects therein.

On the other hand, as a text-book, students or readers not already familiar with the matter would find it difficult to follow, and from this angle the authors might well consider extending the various necessary details in any future edition.

GEO. R. THOMPSON.

INORGANIC CHEMICAL SYMBOLS AND OTHER USEFUL CHEMICAL DATA. By E. R. DARLING. Second Edition. Pp. 119. New York: D. van Nostrand Co. 1927. Price \$1.00.

This little book, compiled by the Professor of Chemistry in the James Millikin University, Illinois, is the outcome of a series of articles in *The Chemical Engineer*. It belongs to the class of laboratory shelf books, and its aim is best indicated by the examples, cited in the Introduction on "Chemical Colloquialisms," of the way in which two workers in different industries will describe the same chemical compound by different names, and the necessity for preventing the confusion which may thus arise. For this purpose classified lists of the chemical compounds of 21 of the more common metals have been made. For instance, there are eleven names under the heading aluminium sulphate, and 21 under arsenious oxide. In this connection it is surprising to note that muriate of lead is given as a synonym of lead sulphate, as well as of lead chloride.

In addition to these lists of inorganic metallic compounds, the book also contains a list of miscellaneous synonyms, together with tables required for frequent reference, including atomic weights, temperature and specific gravity equivalents, standards of weights and measures, and physical properties of metals.

It is a useful little book, the value of which might be still further enhanced by the inclusion of French and German synonyms.

EDITOR.