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An Investigation into the Chemistry of the Reinsch Test for Arsenic and Antimony, and its Extension to Bismuth.*

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PART I.

THE initial work for this research was carried out with a view to finding a method for the separation of small amounts of arsenic from antimony when separating of the latter element from copper (Completed method, ANALYST, 1922, **47**, 1). In view of the rather perplexing results obtained in the qualitative examination, it seemed desirable to investigate further the reactions involved.

SUMMARY OF PREVIOUS WORK.—The literature of the Reinsch test does not appear to be extensive; the following are the principal papers, that could be traced, dealing with the chemistry of it:—

Reinsch's original memoir was published in 1841 in the *J. prakt. Chem.* (**24**, 244) and another in the *Neuer Jahresbericht der Pharmacie* (**16**, 135). The first-named is entitled "On the behaviour of solutions of arsenic and antimony and the metals towards copper"; in it he states the method of using the test, attempts to determine the limits, and goes into the question of the identification of the arsenic obtained in the film. One feature of the paper is an outline of the tests carried out in the cold over a period of several weeks, under which conditions he found that the reaction in dilute hydrochloric acid was much more rapid than in strong, which difference disappeared on heating; he states also that, under these conditions, access of air causes acceleration—a surprising result which is certainly not borne out at higher temperatures. He explicitly states that hydrochloric acid is necessary to the test, and that the reaction will not take place in sulphuric or

* Communication from the Research Department, Woolwich.

acetic acids; this statement appears to have been lost sight of latterly.   He was also familiar with the fact that bismuth as well as antimony gives the test. Throughout he appears to have been under the impression that the arsenic is deposited as element; it is possible that this may have been the case with his films deposited in the cold, as these seem to have differed in appearance from the ordinary film.   A somewhat curious assertion occurs in this paper to the effect that tin and lead in hydrochloric acid solution of certain concentrations and in the presence of air, but not otherwise, will deposit on copper in a powdery form when allowed to stand for some days.   No confirmation of this statement, which on the face of it seems improbable, could be obtained.

Bettendorf states (*Zeitsch. für Chem.* (2), **5**, 492) that the hydrochloric acid used for the test must not be weaker than sp. gr. 1·1.   This is not borne out by experience.

Fresenius, in a paper before the Chemical Society (April 15, 1844), mentions the Reinsch test, drawing attention to its difficulties, but only as an introduction to a test of his own.

Lippert's paper (*J. prakt. Chem.*, **81**, 168) deals solely with the composition and properties of the deposit formed by arsenic in the Reinsch test, to which deposit he ascribes the composition Cu_5As_2.

Drinkwater states (ANALYST, 1883, **8**, 241) that selenium deposits on copper from hydrochloric acid solution in the same manner as arsenic.

Macallan points out that a deposit of copper sulphide might be obtained in testing decomposing organic matter for arsenic (ANALYST, 1883, **8**, 46).

J. L. Howe and P. S. Mertius published "Notes on Reinsch's test" (*J. Amer. Chem. Soc.*, 1896, **18**, 953), in which the following statements were made:—(1) All arsenic compounds soluble in hydrochloric acid give a deposit immediately on heating.   (2) Commercial "metallic" arsenic readily gives the deposit.   (3) Bright crystals of freshly sublimed "metallic" arsenic give no deposit.   (4) Arsenates deposit only after several minutes heating.   (5) In the presence of nitric acid or chlorates there is no deposit owing to the copper dissolving.   (6) Presence of organic matter does not affect the result.

J. St. G. Gray (*Chem. News*, 1871, 73) recognised four metals: arsenic, antimony, bismuth and mercury, as answering to the test, and stated that mercury could be distinguished from the other three, because it could be removed from the copper by rubbing the latter with gold.

John Clark read a paper on improvements in Reinsch's process before the Chemical Society, May, 1893.   This deals with minor details only.

In the first confusion caused by the arsenic scare of 1900, the Reinsch test was recommended by the Expert Committee of the Manchester brewers as a rapid method of sorting large numbers of samples of beer, sugar, etc.

QUALITATIVE TESTS.—In searching for a method of separating small quantities of arsenic from small quantities of antimony it seemed desirable to investigate thoroughly the conditions (*e.g.* as to reaction, presence of other reagents, etc.) under which these two elements are deposited on copper.   This qualitative trial

was carried out as follows:—Slips of copper foil were cleaned with nitric acid (sp. gr. 1·2) and placed in small beakers, about 10 c.c. of dilute solution of arsenious oxide or tartar emetic added, and the whole heated on a plate.

The following results were obtained:—

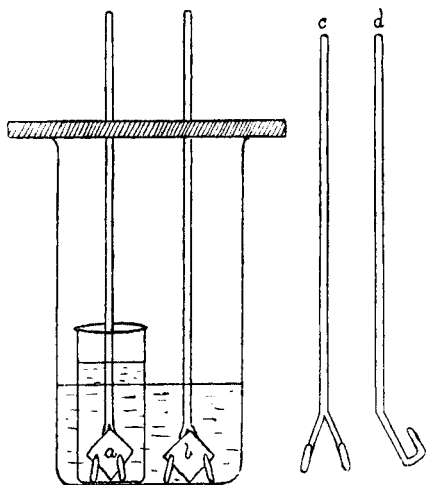| Reagent tried	Antimony	Arsenic
Sodium hydroxide	No deposit	No deposit
Ammonia solution	No deposit	No deposit
Tartaric acid	No deposit	No deposit
Tartaric acid with sodium hypo-phosphite	No deposit	No deposit
Phosphoric acid	No deposit	No deposit
Phosphoric acid with sodium hypo-phosphite	No deposit	No deposit
Sulphuric acid	No deposit	No deposit
Sulphuric acid with sodium hypo-phosphite	No deposit	No deposit
Sulphuric acid + sodium chloride	Immediate deposit	Immediate deposit
Phosphoric acid + sodium chloride	Slight delay	Immediate deposit
Tartaric acid + sodium chloride	Slight delay	Slight delay
Oxalic acid + ammonium chloride	Very considerable delay	Considerable delay
Ammonia + ammonium chloride	No deposit	No deposit
Acetic acid + ammonium chloride	Slight delay	Considerable delay
Ammonium chloride made acid with one drop of acetic acid	Slight delay	No appreciable deposit; after 30 mins. the addition of a few drops of acetic acid brought the arsenic down in two or three minutes
Ammonium chloride + ammonium nitrate made strongly acid with acetic acid	Prompt deposit	Prompt deposit
Copper nitrate pptd. with ammonia acidified with acetic acid	No deposit	No deposit
Acetic acid + potassium iodide cold	Deposit slowly formed	No deposit
Acetic acid + potassium iodide warmed	Prompt deposit	Deposit slowly formed
Acetic acid + potassium iodide warmed with a little iodine	Fairly prompt deposit	Very slight deposit after some time
Potassium cyanide (strong solution) boiled	Immediate deposit	Very slight deposit very slowly formed
Potassium cyanide + cuprous chloride	Deposit rather slower	

It may be mentioned in passing that the reactions with potassium iodide and acetic acid and with potassium cyanide were tried somewhat exhaustively with a view to getting a quantitative separation of antimony and arsenic, but without result, as they did not appear to go to completion.

It will be noticed from the above reactions that there appear to be two essentials to the Reinsch test:—(a) Halides; (b) a certain amount of hydrogen ion.

With a view to determining the influence of the various factors, it was decided to attempt a set of measurements of the reaction velocity with varying amounts

of sodium chloride, sulphuric acid, and arsenic, antimony, or bismuth, as the case might be. The method adopted was as follows:—

APPARATUS.—A 300 c.c. beaker was fitted with a cover made from a cork plate; through two holes in the cover, about an inch apart, passed two glass rods, and at the bottom end of each rod was a fork formed by fusing on two thinner rods, the fork being at about 30° to the axis of the main rod; the end of each prong of the forks was bent upwards to form a hook. One of these hooked forks dipped into the 300 c.c. beaker, the other into a small 20 c.c. beaker standing on the bottom of the larger one. The outer beaker contained the solution to be tested, the inner one distilled water; the hook dipping into the outer beaker supported a slab of cleaned and prepared electrolytic copper, that dipping into the inner beaker a slab of an alloy used as a standard and varying according to the element being investigated. (See diagram.)

PROCEDURE.—The solution to be tested (as a rule 100 c.c.) is placed in the larger beaker, with a fragment of porcelain to ensure steady boiling, the small beaker containing water is lowered into position excentrically, and the whole covered with a glass and set to boil on the plate. The slab of electrolytic copper is prepared by cleaning it thoroughly with nitric acid (sp. gr. 1·2), rinsing, drying and polishing it on fine emery paper, and finally again rinsing it to remove any adherent particles. The standard to be used is then placed in one glass holder and the electrolytic copper in the other, and both are lowered into a beaker containing boiling water acidified with a few drops of sulphuric acid and left there till the solution in the test beaker is boiling; the glass holders, together with the cork plate and the two slabs, are then lifted from their containing beaker and plunged into the beaker containing the test solution in such a way that the holder containing the standard rests on the bottom of the inner beaker, while that containing the copper slab rests on the bottom of the outer beaker, and is therefore immersed in the test solution. The number of seconds which elapse before the colours of the two slabs match is carefully noted. With regard to the preparation of the copper slab the polishing, though not essential, seems to result in far more concordant results and far better colours; apparently the better the polishing the more certain the reading; this point will be referred to again later.

The following were found to be the best standards for this method, and were used throughout:—

Arsenic   70 : 30   Cu As alloy, polished and etched with nitric acid (sp. gr. 1·2).
Antimony 50 : 50   Cu Sb   ,,   ,,   ,,   ,,
Bismuth   90 : 10   Cu As alloy, polished, but not etched; this standard required
                      frequent repolishing.

The comparison was often a matter of some difficulty, and required considerable experience; it was very rarely possible to get an exact match of colours, and it was often necessary to reject experiments owing to the colour or texture of the film being quite different from that of the standard; this was almost unknown in the case of antimony, and seldom occurred in that of bismuth, but arsenic gave a good deal of trouble owing to black or velvety grey films. The aim, of course, throughout was to obtain, not an exact match of the standard, but a point in the course of the reaction which could be identified and noted.

No very definite rules can be laid down on the subject of angle of lighting or angle of observation; the procedure adopted was to arrange the slabs at an angle of 45° to the main direction of the light and observe from a point immediately opposite to them, *i.e.* normal to their surface. It is, however, desirable constantly to shift one's point of observation, looking sometimes at an angle of 45°, or even less, to the surfaces; this is due to the wide variations in the brilliancy and reflecting power of the deposited film. With these precautions, however, and given deposits of the proper colour, concordant readings are easily obtained, at any rate where the time of reaction is small (say under 200 seconds). In dealing with longer times the method is as a rule considerably less accurate, but these longer times occur, generally, on portions of the curves where a very large error in the time makes very little difference to the direction of the curve. The actual matching of the Bi experiments was more difficult than that of arsenic and antimony owing to the paleness of the deposit.

The following results were obtained by this method and plotted as curves:—

INFLUENCE OF VARYING CHLORIDE.—Acid strength kept constant throughout each set of curves; strength of element under examination (*i.e.* As. Sb. Bi) kept constant through each single curve.

Arsenic.

Standard used. 70 : 30 Cu-As alloy polished and etched with 1·2 sp. gr. nitric acid.

In all cases 25 c.c. 1 : 3 sulphuric acid and the necessary amounts of arsenic and sodium chloride made up to 100 c.c.

0·16 grm. As		0·08 grm. As		0·04 grm. As		0·02 grm. As		0·01 grm. As	
NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)
0·10	720	0·20	400	..	..	0·40	470	0·60	430
0·20	260	0·40	270	0·40	340	0·60	370	1·00	360
0·40	185	0·60	200	0·60	240	0·80	230	1·50	290
0·60	120	0·80	160	0·80	180	1·00	190	2·00	230
0·80	90	1·00	135	1·00	160	2·00	120	3·00	170
1·00	75	1·50	80	2·00	85	3·00	85	4·00	140
1·50	50	2·00	65	3·00	60	4·00	70	5·00	120
2·00	40	3·00	45	4·00	50	5·00	60	6·00	110
3·00	25	4·00	40	5·00	45	6·00	55	..	..
4·00	20	5·98	35	..	..	..	..	..	..

Antimony.

Standard used 50 : 50 Cu-Sb alloy, polished and etched with 1·2 sp. gr. nitric acid.

In all cases 25 c.c. 1 : 3 sulphuric acid and the necessary amount of antimony and sodium chloride made up to 60 c.c.

0·10 grm. Sb		0·05 grm. Sb		0·02 grm. Sb		0·01 grm. Sb		0·005 grm. Sb	
NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)
0·15	80	0·15	130	0·15	160	0·15	195	0·20	140
0·20	32	0·20	55	0·20	70	0·20	90	0·25	90
0·25	21	0·40	28	0·25	60	0·25	80	0·30	75
0·40	13	0·60	17	0·40	35	0·40	50	0·35	70
0·60	10	0·80	12	0·60	25	0·60	37	0·60	50
0·80	7	2·00	5	0·80	22	0·80	30	0·80	40
1·50	3	..	..	1·50	17	2·00	25	2·00	35

Bismuth.

Standard used 90 : 10 Cu-As alloy, polished, not etched.

In all cases 10 c.c. 1 : 3 sulphuric acid and the desired quantities of bismuth and sodium chloride made up to 100 c.c.

0·01 grm. Bi		0·02 grm. Bi		0·005 grm. Bi	
NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)	NaCl (Grms.)	Time (Secs.)
Nil	200	..	..	..	..
·05	128	0·05	120	0·20	160
·10	80	0·10	50	0·25	120
·20	70	0·20	40	0·40	90
·50	60	0·40	35	0·60	80
·80	55	..	..	..	..
·90	55	..	..	0·80	75
1·00	55	1·00	33	1·00	75
3·00	55	6·00	25	..	..

INFLUENCE OF VARYING ARSENIC OR ANTIMONY.—Curves for these were plotted from the figures obtained for the preceding set of curves.

In the case of arsenic a few additional points were determined to complete the curves. In all cases 25 c.c. of 1 : 3 sulphuric acid was used, and the bulk made up to 100 c.c.

Grms.	Seconds	Grms.	Seconds
0·025 As 2·00 NaCl }	90	0·044 As 0·40 NaCl }	320
0·024 As 1·00 NaCl }	180	0·024 As 3·00 NaCl }	70

In the above sets of curves the acid strength, though constant throughout each set, varies from one element to another; it will be shown in the following set that at a certain concentration of acid a maximum effect is obtained, and that further addition of acid is without influence. This concentration was well exceeded in all the sets.

INFLUENCE OF VARYING ACID STRENGTH.—In all cases 1·0 c.c. of 1 : 3 sulphuric acid contained 0·456 grm. of H_2SO_4. In this series three curves were plotted for each element; in the second of these the amount of the element was the same as in the first, and the sodium chloride altered, and in the third the sodium chloride was the same as in the first, and the amount of element altered.

Arsenic.

Standard used 70 : 30 Cu-As alloy, polished and etched with 1·2 nitric acid.   In all cases the bulk made up to 100 c.c.

Arsenic	0·16 grm.	Arsenic	0·08 grm.	Arsenic	0·16 grm.
Sodium chloride	2·00 grms.	Sodium chloride	2·00 grms.	Sodium chloride	1·00 grms.
1 : 3 H_2SO_4	Seconds	1 : 3 H_2SO_4	Seconds	1 : 3 H_2SO_4	Seconds
1·0 c.c.	450	2·0 c.c.	260	2·0 c.c.	530
2·0	240	3·0	160	3·0	270
3·0	130	4·0	130	4·0	180
4·0	110	5·0	105	5·0	145
5·0	90	6·0	85	6·0	120
6·0	65	7·0	70	7·0	105
7·0	55	8·0	65	8·0	95
8·0	50	9·0	55	9·0	90
9·0	45	10·0	55	10·0	88
10·0	40	13·0	50	13·0	85
13·0	40				

Antimony.

Standard used 50 : 50 Cu-Sb alloy, polished and etched with 1·2 sp. gr. nitric acid.   In all cases the bulk made up to 100 c.c.

Antimony	0·005 grm.	Antimony	0·005 grm.	Antimony	0·01 grm.
Sodium chloride	0·50 grm.	Sodium chloride	1·00 grms.	Sodium chloride	1·00 grms.
1 : 3 H_2SO_4	Seconds	1 : 3 H_2SO_4	Seconds	1 : 3 H_2SO_4	Seconds
1·0 c.c.	360	0·5 c.c.	470	0·5 c.c.	420
2·0	230	1·0	270	1·0	200
3·0	200	2·0	140	2·0	110
4·0	180	4·0	100	4·0	80
6·0	160	6·0	85	6·0	65
8·0	155	7·0	90	8·0	65
10·0	155	8·0	85	10·0	65
		9·0	90		
		10·0	85		

Bismuth.

Standard used 90 : 10 Cu-As alloy, polished, not etched.   In all cases the bulk made up to 100 c.c.   In stating the amounts of acid, allowance is made for that contained in the bismuth solution.

Bismuth	0·01 grm.	Bismuth	0·005 grm.	Bismuth	0·01 grm.
Sodium chloride	1·00 grms.	Sodium chloride	0·50 grm.	Sodium chloride	0·50 grm.
1 : 3 H_2SO_4	Seconds	1 : 3 H_2SO_4	Seconds	1 : 3 H_2SO_4	Seconds
3·9 c.c.	55	1·8 c.c.	150	3·9 c.c.	60
4·9	40	2·8	80	5·3	45
5·9	40	3·8	65	8·3	45
25·0	40	4·8	50		
		5·8	50		

The bismuth curves were obtained with great difficulty owing to the acid strength being barely great enough to keep the bismuth in solution.   In all three of these sets at a certain concentration of acid, which remains constant for any one element, but varies from one element to another, the curves become horizontal, and further addition of acid is without effect on the rate of reaction.   This point is

For arsenic   Approx. 12·0 c.c. 1 : 3 H_2SO_4 = 5·47 per cent. H_2SO_4.

,,   antimony   ,,   6·0 c.c. 1 : 3 H_2SO_4 = 2·74 per cent. H_2SO_4.

,,   bismuth   ,,   5·0 c.c. 1 : 3 H_2SO_4 = 2·28 per cent. H_2SO_4.

As this point appears to be constant, whether the amount of sodium chloride, or of the element under examination, is varied, it is presumably connected with a change induced in the surface of the copper by the acid.   This will be discussed later.

It had been observed in the course of the qualitative work that the presence of soluble copper salts inhibited the Reinsch reaction; it was thought desirable to investigate this action quantitatively.   The method used was the same as before; the amounts of element, sodium chloride, and acid, were kept constant, and varying amounts of copper sulphate added.

With the higher amounts of copper the colour of the slabs was considerably masked by the blue colour of the solution, and this necessitated withdrawing them momentarily to make comparison; this method appeared to give accurate results.

Arsenic.		*Antimony.*		*Bismuth.*	
Standard 70 : 30 Cu-As alloy		Standard 50 : 50 Cu-Sb alloy		Standard 10 : 90 As-Cu alloy	
As, 0·08		Sb, 0·01		Bi, 0·01	
NaCl, 2·00		NaCl, 1·00		NaCl, 1·00	
1 : 3 H_2SO_4, 25 c.c.		1 : 3 H_2SO_4, 25 c.c.		1 : 3 H_2SO_4, 10 c.c.	
Bulk, 100 c.c.		Bulk, 100 c.c.		Bulk, 100 c.c.	
Cu (Grm.)	Time (Secs.)	Cu (Grm.)	Time (Secs.)	Cu (Grm.)	Time (Secs.)
Nil	35	Nil	47	Nil	60
0·005	45	0·01	65	0·01	70
0·03	60	0·02	110	0·02	100
0·05	80	0·03	200	0·03	150
0·06	90	0·04	320	0·04	270
0·07	110	0·05	530	0·045	630
0·08	160				
0·09	260				
0·10	400	0·10 No trace after 20 minutes			

The most noticeable thing about these curves is the fact that quite a small proportion of copper, as a cupric salt, will stop the reaction altogether; and this limiting proportion for arsenic is quite different from that for antimony; it would seem probable that one could separate arsenic from antimony by having a small percentage of cupric sulphate present.   Another aspect of the case presents itself; it will be shown later that cuprous chloride is one of the principal products of the Reinsch reaction, and it became necessary to find out whether the inhibiting property belonged to soluble copper salts generally, or whether it was confined to cupric salts; obviously, if the former were the case, the Reinsch reaction could never go to completion.   Cuprous sulphate not being readily obtained, it seemed better to produce cuprous chloride from the sodium chloride already in the test solution than to complicate calculations by adding cuprous chloride itself; in addition to this, it was very necessary to avoid adding any copper in the higher state of oxidation, as the inhibiting effect of quite small amounts of this has already been shown.   The following procedure was adopted:—A mixture of 6·0 grms. of sodium chloride, 25 c.c. 1 : 3 sulphuric acid, and 59 c.c. of water was set to boil in the test beaker, and to this, when boiling, was added the weighed amount of cuprous oxide; when this had practically dissolved (but without more

loss of time than could be helped on account of danger of oxidation) 16 c.c. ($=0.08$ grm. As) of the arsenic solution was added, and, as soon as this boiled, the test was carried out in the ordinary way.   The following results were obtained:—

Cu_2O	Time
Nil	35 seconds
0·2 grm.	55 ,,
0·3 ,,	55 ,,

The solution always contained a trace of cupric copper amply sufficient to explain the 20 seconds lag.   Apparently, although most of the cuprous oxide was attacked by the hydrochloric acid to form cuprous chloride, some of it was attacked by the excess sulphuric acid, giving cupric sulphate and metallic copper in the usual way; the evidence for this, apart from the faint bluish colour of the solution, lay in the fact that the trace of copper formed, though resembling cuprous oxide in appearance, was speedily blackened by the arsenic depositing on it when the arsenic solution was added.

When it is borne in mind that a similar amount of copper in the cupric state would (as is seen by reference to the curve) have probably stopped the reaction altogether, or have, at any rate, slowed it down to hours instead of seconds; and also that the increase from 0·2 grm. to 0·3 grm. of cuprous oxide is attended by no measurable increase in the time of reaction, it seems fair to draw the conclusion that cuprous salts have no inhibiting action on the Reinsch reaction.   The following results were obtained for antimony and bismuth by the use of a similar method:—

Bismuth.   A trial was made with 0·02 grm. Bi, 2·0 NaCl, 25 c.c. 1 : 3 H_2SO_4 and 0·2 grm. of Cu_2O per 100 c.c.

This gave a reading of 90 secs. (30 secs. without cuprous oxide).   There was, however, considerable difficulty in dissolving the cuprous oxide, an appreciable amount of metallic copper being left on the bottom, corresponding, of course, to a similar amount of cupric salt in solution.   A second test was accordingly made with 0·02 grm. of bismuth, 6·0 grms. of sodium chloride, 20 c.c. of 1 : 3 sulphuric acid, and 0·3 grm. of cuprous oxide, which gave the following results:—

Cu_2O Grm.	Seconds
0·30	30
Nil	25

Antimony.   0·02 grm. Sb, 6·0 grms. NaCl, 20 c.c. 1 : 3 H_2SO_4, made up to 100 c.c.

Grm.	Seconds
0·30 Cu_2O	30
Nil	25

A necessary precaution to be taken in all use of the Reinsch reaction, either qualitatively or quantitatively, at once suggests itself.   Since cuprous chloride is necessarily present in the solution as a product of reaction, and since cupric salts are fatal to the reaction, it is very necessary to ensure that the cuprous chloride does not get oxidised in any way, even slightly.   So far as the author is aware, this precaution, up to the present, has been neglected and the matter left to chance.

PRODUCTS OF REACTION.—Deposits were obtained in a form that easily flaked off the copper. This is the normal state of things with arsenic and bismuth; the case of antimony will be dealt with later. The deposits were washed thoroughly with water, then with alcohol, and dried rapidly in an electric oven. Details of the analyses are as follows:—

Arsenic.—The sample (0·5000 grm.) was dissolved in dilute sulphuric acid and hydrogen peroxide. Solution boiled, excess of tartaric acid added, liquid made strongly alkaline with caustic soda, sulphuretted hydrogen passed. Copper separated as sulphide, ultimately titrated with sodium thiosulphate. Arsenic in filtrate separated as sulphide in solution acidified with sulphuric acid, ultimately titrated with iodine.

	Grm.	Per cent.	Percentage composition of Cu_5As_2
Copper	0·3300 =	66·00	67·74
Arsenic	0·1673 =	33·46	32·26
		99·46	100·00

This analysis seems to indicate that a certain amount of the element arsenic is deposited electrolytically, in addition to the compound Cu_5As_2.

Bismuth.—The sample (0·3728 grm.) was dissolved in dilute sulphuric acid and hydrogen peroxide, solution boiled, neutralised, and bismuth thrown down as basic carbonate with ammonium carbonate, according to the usual procedure, and weighed as Bi_2O_3. *Result*: Weight of Bi_2O_3, 0·4140 grm.; bismuth, 99·50 per cent. Only a trace of copper was found in the filtrate from the bismuth carbonate.

Antimony.—The case of this element is much more complicated than the foregoing. If copper is boiled with a mineral acid solution of antimony containing chlorides, the first effect observable is the formation of a purple film on the copper, the colour of which corresponds with that of the compound Cu_2Sb. On continuing the boiling, bluish-white flecks appear on the purple and these spread until the entire surface is coated with a uniform white film; after this no further colour change takes place. If the white film has been produced in not too strongly acid a solution, it will be found, on removal from the liquid, that it is strongly adherent, and will take a brilliant polish; if, however, strong hydrochloric acid has been used the film flakes off readily, leaving a clean surface of copper underneath. If the white film is heated with trichloracetic acid solution it turns purple; this is apparently due merely to the solution of the white constituent. Conversely, if the film is deposited in a solution of trichloracetic acid and sodium chloride, it remains purple, but deposition in this case is slow, the film is, as a rule, fairly closely adherent, and the copper dissolves away somewhat rapidly.

Many attempts to get a pure detached sample of either the white, or the purple, films uniformly resulted in failure. The following analysis was carried out on a sample which was quite obviously a mixture of the two varieties:—A weighed quantity (0·3045 grm.) was dissolved in hydrochloric acid and potassium chlorate,

chlorine boiled off, sulphurous acid added and the excess boiled off; excess of Rochelle salt added, the whole made strongly alkaline with sodium hydroxide, and hydrogen sulphide passed through the liquid for a considerable time. The copper sulphide precipitate was filtered off, ignited and redissolved in nitric acid, and the copper estimated by titration with thiosulphate solution. The filtrate was acidified, the antimony separated as sulphide with the usual precautions, the sulphide dissolved in sodium peroxide solution, the solution boiled and acidified with hydrochloric acid, and the antimony estimated by Rowell's method. *Results.—* Antimony, 75·8; copper, 24·6 per cent.; (total, 100·4 per cent.).

There appear to be only two compounds of copper and antimony known— Cu_3Sb and Cu_2Sb. The percentage compositions of these two compounds are as follows:—

			Cu_3Sb	Cu_2Sb
Antimony	..	..	38·83	48·78
Copper ..	..	..	61·17	51·22

It will be noted that the percentage of antimony in the film is considerably higher than either of these, and therefore it would seem that the deposition of the purple film is followed by that of pure antimony, probably electrolytically. There seems no reason to doubt, in view of its appearance, that the purple film is the compound Cu_2Sb; there is no evidence whether or no Cu_3Sb also comes down.

In all three cases a considerable amount of copper goes into solution as cuprous chloride, but the solution remains colourless unless oxidation takes place.

In the case of arsenic no evolution of hydrogen arsenide appears to occur.

(To be continued.)

Determination of the Purity of Vanillin.

By S. B PHILLIPS, A.I.C.

(Read at the Meeting, March 7, 1923.)

THE methods introduced in the following paper are intended for the determination of the purity of crystalline vanillin. No attempt has been made to estimate vanillin in vanilla extract.

A very large proportion of the vanillin on the market at present is synthetic, and adulterants may be added which the present methods of estimating vanillin do not detect. Such criteria as melting point and solubility in various solvents are resorted to, but further tests are then required to determine the percentage of the impurity.

In chemical constitution vanillin contains three characteristic groups, any one of which may be estimated and the result interpreted as weight or percentage of vanillin. Of the early methods suggested, Welman's consisted in the direct

titration of the hydroxyl group with standard alkali, with the use of phenol-phthalein as indicator. In practice it was suggested that an excess of standard alkali should be added, and the excess determined by titration with standard acid. Unfortunately, such a simple method proved useless when an accurate result was required, the end-point of the titration being very unsatisfactory. Moreover, the addition of an acid adulterant, such as benzoic acid, raises the result, and this may then be corrected by the addition of a neutral adulterant.

The more recent methods suggested all aim at the estimation of the aldehyde group by quantitative precipitation with various reagents, the methods being gravimetric. Certain colorimetric methods have also been recommended for the estimation of vanillin in extracts. In the gravimetric estimations p-nitro- and p-bromphenyl-hydrazines, β-naphthyl-hydrazine (1) and m-nitro benzoyl-hydra-zide (2) have been used. Of the phenyl-hydrazines, Feinberg prefers the p-nitro derivative (3), but the author has found that the results obtained with this reagent are usually high, probably owing to the slight decomposition of the reagent, ac-companied by the precipitation of a compound which is filtered off and weighed together with the vanillin p-nitro-phenyl-hydrazone. p-Bromphenyl-hydrazine is still less stable. The hydrazines seem to have the common disadvantage of being more or less unstable. m-Nitro-benzoyl-hydrazide could not readily be obtained, and this reagent was therefore not tested. Gravimetric methods of this type are open to the disadvantage that, in the presence of aldehyde substances, such as piperonal, correct results are not obtained, the aldehyde impurities being precipitated together with the vanillin, and the result therefore being too high.

The third group which may be estimated in vanillin is the methoxy group, which is estimated by means of Zeisel's method of distillation with hydriodic acid of constant boiling point, but the method is much too long to be of practical value.

The methods to be described give correct results in nearly all cases.

VOLUMETRIC ESTIMATION.—This method is an alkali titration method for the estimation of the hydroxy group. In principle the method is as follows:—Vanillin and p-toluidine are dissolved together in 80 per cent. alcohol. An anhydro derivative—$(OH)(OCH_3)C_6H_3CH=N \cdot C_6H_4CH_3$—is obtained which gives a yellow solution. This compound contains the original hydroxyl group of the vanillin, and is therefore soluble in alkali. A measured excess of standard alkali is added, followed by a comparatively large volume of cold water. Addition of standard acid first neutralises the excess of alkali, and then liberates the anhydro derivative from its sodium salt. The first drop of acid which liberates the derivative from its salt gives a yellow turbidity, the free derivative being practically insoluble in the liquid. The volume of alkali required for the titration of the vanillin is thus obtained.

In detail the method is as follows:—About 1 grm. of vanillin (between 0·95 and 1·05 grm.) is weighed into a 250–300 c.c. flask, and 20 c.c. of 80 per cent. alcohol (sp. gr. 0·8484) are added from a pipette. This alcohol must be neutral to methyl red, free from aldehydic and ketonic substances, and from oils which

give a turbidity on the addition of water. At this stage acid substances are neutralised. Two drops of a 1 per cent. solution of methyl red are added, and 0·1 N sodium hydroxide solution is run in, drop by drop, until the red colour is completely discharged. If more than 5 c.c. of 0·1 N are required, the estimation must be repeated with the use of stronger alkali. Methyl red indicates organic acids, but does not give an acid reaction with vanillin. The red colour having been dis charged, another drop of indicator is added, and the titration continued, if necessary. To the neutralised solution are now added 1·1–1·2 grms. of pure p-toluidine (see note on purification), and, after this has dissolved, 20 c.c. of 0·5 N sodium hydroxide are added from a pipette, followed by 100 c.c. of cold distilled water, free from carbon dioxide. In practice, 90 c.c. of water are added, and the temperature of the solution is adjusted as rapidly as possible to between 15° and 17° C. This attained, the remaining 10 c.c. of water are poured in down the thermometer stem. Prolonged exposure of the solution to the air before the titration should be avoided, owing to the absorption of carbon dioxide. The appearance of a precipitate on the addition of the water indicates the presence of an aldehydic compound in which no phenolic hydroxyl group is present, such as piperonal. Such compounds readily form anhydro derivatives with p-toluidine, but these are insoluble in aqueous alkali. If a precipitate forms, the estimation must be dis-continued and resort made to the alternative method described later. If the liquid remains clear, 0·5 N sulphuric acid is run in from a burette, until one drop causes a permanent turbidity. The approach of the end-point is indicated by a gradual deepening of the yellow colour as the last c.c. of acid is run in. The difference between the volumes of acid and alkali represents the volume of 0·5 N alkali required for the titration of the vanillin taken. One c.c. of 0·5 N sodium hydroxide solution represents 0·076 grm. of vanillin.

Accurate results are obtained, in the case of benzoic acid as adulterant, with quantities up to 10 per cent., but with higher percentages of acid it is advisable to adopt the gravimetric method to be described. Amongst numerous samples of vanillin examined during the course of the present research, no sample of first-class vanillin was found to contain more than 1 per cent. of acid estimated as vanillic acid, although some of the samples had been kept in cardboard con-tainers for ten years. Oxidation of vanillin due to exposure to the air proceeds extremely slowly (*vide infra*).

The following figures were obtained with benzoic acid as adulterant:

Percentage vanillin found	Actual percentage
96·5	96·5
89·0	89·2

Incidentally it may be mentioned that the burette readings must be taken as accurately as possible. The author has found that good results are obtained by using a 10 c.c. burette, as the volume may be read to 0·02 c.c. This is necessary, owing to the high molecular weight of vanillin.

GRAVIMETRIC METHOD.—The vanillin is precipitated as the semi-carbazone from dilute acetic acid solution. The precipitate is a very convenient one to

work with, on account of easy washing and filtration, and it may be dried in a water-oven for six or eight hours without losing a weighable quantity by volatilisation.

The following is the method adopted in the absence of such compounds as piperonal, as indicated in the volumetric estimation:—One grm. of the sample is weighed into a small beaker of about 100 c.c. capacity, and 13·6 c.c. of 0·5 N sodium hydroxide solution are added from a burette. This gives a very slight excess of alkali. The liquid is warmed slightly on a water-bath and shaken to effect solution. Into a beaker of similar capacity are weighed 2·4 grms. of semicarbazide hydrochloride, i.e. 3–4 equivalents, and 3·0 grms of anhydrous sodium acetate, or the equivalent of the crystalline salt (5·0 grms.) are added, together with 30 c.c. of water, and the salts dissolved by warming and stirring. This solution is filtered into the warm vanillin solution and, after stirring, the mixture is heated by immersing the beaker in a boiling water-bath for ten minutes. After the liquid has cooled, the precipitation is allowed to continue in the cold for four hours.

In the meantime a 12 cm. filter paper is dried in a water-oven for at least one hour, folded, placed in a stoppered weighing bottle and immediately weighed. After four hours' standing the precipitate is filtered on to the weighed paper, and washed with cold water until the filtrate gives no precipitate with silver nitrate solution. The filtrate and washings should not exceed 200 c.c. in volume. The filter and funnel containing it, are placed in a water-oven and, after one hour, the paper and the precipitate are removed from the funnel, placed in a porcelain basin, allowed to remain in the oven for a further 2 to 3 hours, then placed in the weighing bottle and weighed immediately. This method of weighing the filter paper and precipitate has been found very efficient, and gives much more accurate results than are obtained by weighing the paper alone or by counterpoising with a similar paper. The precipitate is heated for a further hour and re-weighed, etc., until the weight is constant.

The weight of semi-carbazone multiplied by 0·7271 gives the weight of vanillin.

If an impurity such as piperonal is present, a modification of this method is necessary. The vanillin is separated from these substances by dissolving the semi-carbazone in ammonium hydroxide solution. Vanillin semi-carbazone, by virtue of its hydroxyl group, forms a soluble ammonium salt which gives a yellow solution, whilst piperonal semi-carbazone is insoluble. The precipitate, obtained as above, is weighed, carefully removed from the paper, and placed in a beaker of about 200 c.c. capacity, 60 c.c. of water and 40 c.c. of ammonium hydroxide solution (sp. gr. 0·880) are added, and the mixture is heated to about 50° C., and thoroughly stirred to break up any masses that may be present. After cooling, the liquid is filtered through a dried and weighed filter-paper, prepared as previously described, and the undissolved portion is washed with cold distilled water until all of the yellow colour has been removed. As a test to show whether the solution of the vanillin semi-carbazone has been

completely effected, the paper and precipitate are washed once with dilute ammonium hydroxide solution (one volume of 0·880 ammonium hydroxide diluted with two volumes of water).   The reappearance of a yellow colour indicates that solution is not complete.   In this case washing with cold water is repeated to remove the vanillin semi-carbazone salt, and the insoluble portion is again tested. When found to be free from vanillin semi-carbazone, the precipitate is washed, dried for three hours in a water-oven and weighed.   The weight of insoluble semi-carbazone thus obtained is deducted from the original weight of the mixed semi-carbazones, and the remainder is calculated to vanillin.

In actual estimations, in which piperonal was added to vanillin, the following results were obtained:

Percentage of vanillin found	Actual percentage
89·4	89·2
87·7	87·5

The only method that could be found in literature for the estimation of vanillin in the presence of piperonal was that of Hanuš, in which the vanillin is quantitatively precipitated with platinic chloride (4).

The sample of vanillin on which the investigation was carried out was prepared by purifying a good commercial synthetic sample.   The vanillin was dissolved in very dilute sodium hydroxide solution, the liquid filtered and treated with carbon dioxide.   Owing to the solubility of vanillin in sodium carbonate solution, precipitation was very difficult, and was finally effected by cooling the solution to 2° C. and passing in a rapid current of carbon dioxide.   The precipitated vanillin was filtered off, washed free from carbonate, etc., and recrystallised from 30 per cent. alcohol.   Large crystals were obtained which were dried in a vacuum desiccator over sulphuric acid.   The sample gave the following figures by the estimation of the various groups:

	Vanillin per cent.
Methoxy group (Zeisel)	99·5
Aldehyde group (semicarbazone)	99·4
Hydroxy group (titration)	99·3

The p-toluidine used in the volumetric process was very crude when supplied, and recrystallisation did not improve it to any appreciable extent.   A good sample was obtained by distilling the commercial product with steam and recrystallising it from 20 per cent. alcohol.   The crystals were dried by spreading them on a filter paper, covering them with a second paper and allowing them to stand thus exposed to the air for several days.

Of the methods detailed above, it is rarely necessary to resort to the gravimetric process.   The methods, however, do not entirely exclude all possibility of adulteration.   Coumarin is not detected in the volumetric process.   It is a lactone, and, therefore, has acid properties, sufficiently strong to interfere in the titration, but not strong enough to be detected by the methyl red indicator.   In the case of coumarin the odour of the sample is a good criterion and, if it is suspected as an adulterant, the gravimetric method should be used.

OXIDATION OF VANILLIN.—The possibility of the oxidation of vanillin to vanillic acid by exposure of the crystals to air, was investigated. Samples of purified vanillin were exposed to air, moisture and light, and occasionally to direct sunlight for a period of one month, but the increase in the percentage of acidity during this period was practically negligible. With the vanillin in solution oxidation due to exposure to the air proceeds much more rapidly. It was found, in the course of the research, that solutions of vanillin in alkali behave similarly to alkaline pyrogallate solution. A solution of vanillin in sodium hydroxide or sodium carbonate solution changes to a brown colour in several hours, the colour gradually deepening, until, after 24 hours, the solution is practically black. This is apparently due to complete decomposition of the vanillin. Out of contact with the air no such change could be detected in 24 hours. A solution of vanillin in water did not change in colour on exposure to the air for 24 hours, and, moreover, no increase in acidity could be detected.

MELTING POINT.—The melting points of some of the compounds produced were determined:

Vanillin semi-carbazone	232°C. (corrected for exposed stem).	
Piperonal semi-carbazone	218°C.	,, ,, ,, ,,
Vanillin p-nitro-phenyl-hydrazone	223°C.	,, ,, ,, ,,
Vanillin p-brom-phenyl-hydrazone	148°C.	,, ,, ,, ,,

In conclusion, the author wishes to thank Messrs. Cadbury Bros. Ltd., for permission to publish the above research, which was carried out in their research laboratory at Bournville.

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DISCUSSION.

Mr. H. E. BURGESS congratulated the author on bringing before the Society a very careful and interesting piece of analytical work, but said that it was somewhat doubtful whether it was necessary to make careful volumetric or gravimetric estimations of synthetic vanillin, for he was of opinion that the melting point was quite sufficient to indicate any of the adulterants which had been suggested. Vanillin made from iso-eugenol or guaiacol could easily be produced of a very high degree of purity, giving a very sharp melting point, which would be lowered by practically any adulterant which might be used. It would be interesting to know whether there was any method by which iso-eugenol vanillin or guiacol vanillin could be differentiated. To an expert, the difference in odour was quite perceptible, but for the general analyst some more definite means was desirable.

Mr. E. T. BREWIS said that his views corroborated those of the last speaker, and that vanillin was purchased for the sake of its flavour. It was usual to determine the melting point. Acetanilide was a common adulterant, and piperonal

was known to be added to vanillin in some cases. In comparing different samples of vanillin he had found it a useful practice to "break down" the samples with large amounts of sugar, and for several observers to compare the tastes of the different samples. As a rule, people preferred to have a vanillin that was less pure than 99·5 or 99·6 per cent., because it had a better flavour. He asked whether the author had noticed any difference between vanillin prepared from eugenol and vanillin prepared by the guiacol process. People in the trade were very skilful at adding improving agents, to give a "bouquet," and the tendency of these was to give a "pretty" odour rather than a true one. He added that some of these vanillins were perfectly white, and that others, again, were of a cream colour. He considered the cream-coloured samples of vanillin to be generally preferable to the pure white ones.

Mr. M. S. SALAMON asked what the experimental errors in this process were, and whether it could be used to distinguish between a vanillin of 99·5 per cent. and one of 99·9 per cent. purity. He also asked whether the author had noticed any difference, when using this process, between vanillin that gave a very slight colour with concentrated sulphuric acid solution and those giving quite an appreciable colour.

Mr. S. B. PHILLIPS, replying, said that the melting point was always a very useful and important factor to go by, but gave no indication of the nature of the impurity or adulterant. The melting point was usually under 80 to 82° C. As regard adulterants, the addition of 5 per cent. would prove quite a profitable business. The analytical figure was not generally taken as the final test for flavour; a sample giving 99·5 per cent. might be more desirable than one giving 99·9 per cent., supposing the impurity were sugar; the usual impurities were, owing to smell, more noticeable. The gravimetric method should show the difference between 99·5 per cent. and 99·9 per cent. As regards the colour with sulphuric acid, the amount of impurity caused a very distinct difference, 2 per cent. of sugar, for instance, gave a dark colour; perhaps the nature of the vanillin prevented the formation of such a dark colour in the case of other compounds.

The Quantitative Estimation of Hemp and Wood Fibres in Paper Pulp.

BY W. DICKSON, F.I.C.

(Read at the Meeting, May 2, 1923.)

INTRODUCTION.—In examining papers of any new make and origin it is very necessary that the analyst should be able to estimate with a reasonable degree of accuracy the proportion of different kinds of fibre in a given sample of paper. Generally speaking, there is little help to be obtained from the literature on this subject. Some authors state that a great deal of experience is required to estimate with any approach to accuracy the quantity of various fibres contained in paper,

and that the experienced man can judge the amounts from a cursory examination of a slide under the microscope more accurately than an inexperienced person from elaborate counts of the fibres.

Differential staining with iodine and zinc chloride, etc., is not of much serv e in bringing out the different classes of fibres, because differential staining depen s upon the sensitiveness of the cellulose to hydration. This sensitiveness deper is to some extent on the treatment to which the fibre has been subjected, as well as **on its** origin. As regards these staining methods, the author agrees with Clapperton (*Practical Paper Making*, p. 163), and holds that micro-structure is the only safe criterion upon which to base a diagnosis of the constituents of paper pulp.

The difference in micro-structure of the various fibres is often very difficult to recognise, and undoubtedly a very great deal of experience is required in order to make reliable diagnosis of the types of fibres present in the mixtures. There is no difficulty in recognising the majority of woody cells under the microscope. There are, however, in pure wood fibre a number of cells (see Figs. 3 and 4) which are decidedly difficult to distinguish from fibres, say, of hemp and manilla, and it is the presence of these fibres which makes the quantitative estimation of the amount of hemp and wood in a mixture so very difficult.

It will be readily understood that in order to make a quantitative estimation of these two fibres it is necessary to count the number of fibres of each kind in a large number of fields and, unless the operator can decide definitely on each fibre examined, results are liable to be very doubtful.

IDENTIFICATION OF FIBRES IN PAPER PULP.—The first step towards a quanti-tative estimation of fibres, therefore, is to ensure a quick and certain recognition of different fibres under the microscope. It was found that Cross and Bevan's double staining method, in which malachite green and Congo red are used, brought out structural details very well, and it was adopted. Generally the whole of the fibre is dyed a deep reddish brown, but there appear occasional green fibres. It is concluded that these fibres have been highly lignified, and have therefore taken the malachite green most readily. This stain probably gives an idea of the completeness or otherwise of the bleaching of the fibres, but no attention is paid to these different colours as a means of identification of the fibres. The stain was adopted simply because it appeared to bring out the detail in the micro-structure very well.

In making slides for examination it is necessary to ensure that the fibres shall be well spread out over the cover slip, so that individuals may be easily seen and counted. To do this it was found best to work with a dilute mixture of pulp and water. The concentration 0·02 to 0·03 per cent. recommended by Spence and Krauss (*World's Paper Trade Review*, Dec. 18th, 1917) was found very suitable. The stained pulp in the proper concentration is placed in a cylindrical glass vessel, and stirred with a microscopic teasing needle. The needle is held stationary near the side of the glass for a minute or two, with the result that the fibre attaches itself to the needle and a good representative sample can be
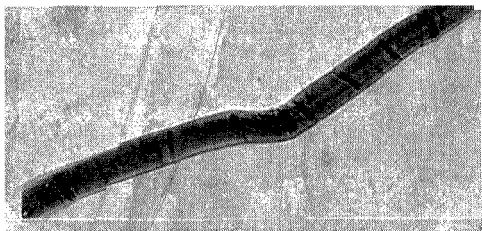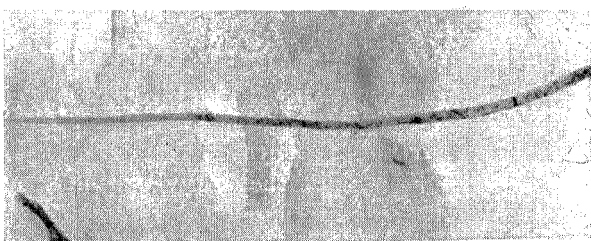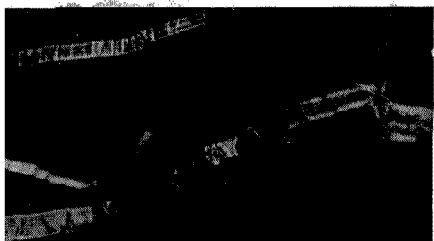
FIG. 1.   × 320 diams.

FIG. 3.   × 67 diams.

FIG. 2.   × 227 diams.
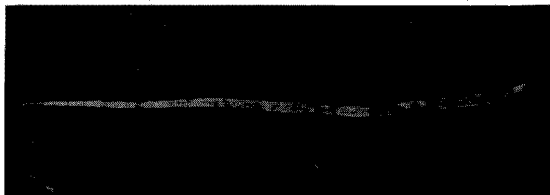
FIG. 4.   × 67 diams.

FIG. 5.   × 63 diams.

FIG. 7.   × 67 diams.
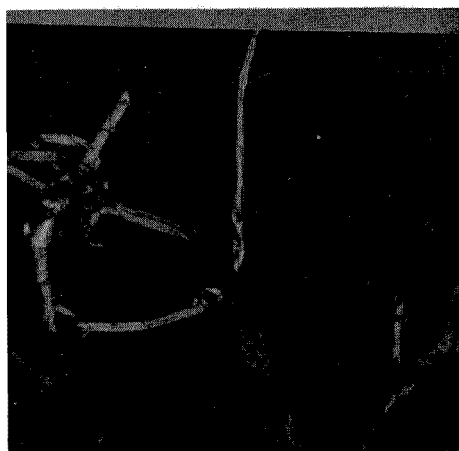

FIG. 6.   × 63 diams.

FIG. 8.   × 67 diams

Plate W. Dickson's Paper.

withdrawn.   The sample is placed on a cover slip and well teased out, so that the individual fibres can be seen and counted.   During the teasing, part of the sample is rejected and care is taken to make this rejection uniform throughout, so that a good representative sample is retained on the cover slip.   The slip is dried with alcohol and mounted in Canada balsam in the usual way.   The slide is examined under a microscope fitted with the usual Nicol prisms to provide polarised light. In examining fibres with a view to determining their kind it was found most useful to examine both by ordinary light and polarised light.

From the photo-micrographs shown in this paper it will be seen that certain characteristic markings of different fibres are brought out best in ordinary light, and certain others in polarised light.   For example, the cross markings in hemp (Fig. 5) are most readily seen by ordinary light, but there is a peculiar characteristic appearance of hemp fibres which is best brought out by polarised light (see Fig. 6). With practice the operator becomes very expert in noting these different appearances on rotating the Nicol prisms attached to the sub-stage polariser of the microscope.   As far as the author is aware, examination by means of polarised light has not previously been utilised for the identification of fibres in paper pulp.

For purposes of identification of fibres it is useful to employ two magnifications, say, 100 diam. and 400 diam.   With practice, 100 diam. is sufficient, but for purposes of confirmation the higher magnification is convenient.

Figs. 1 and 2 show photo-micrographs of characteristic hemp fibres under the high power, with and without polarised light.   Figs. 5 and 6 show hemp fibres under the low power, with and without polarised light.   Figs. 7 and 8 show mixtures of 80 per cent. of hemp and 20 per cent. wood.   These figures illustrate very well the structure of the hemp and wood, and it will be readily seen how the different fibres can be picked out when necessary.

The photomicrographs shown were all made from pulp prepared in the laboratory, from known raw materials.   The method of preparation of the pulp was as follows:—A quantity of the raw material, say 50 grms., of hemp rope, was boiled with 10 per cent. sodium hydroxide solution for several hours, the liquid filtered through a Büchner funnel, and the residue pulped in a mortar.   The resulting mixture was boiled up with an acid sodium sulphite solution and again filtered, pulped, and thoroughly washed.   The pulp was then in a fairly well disintegrated condition ready for bleaching, which was done by warming with sodium hypochlorite.   This solution was acidified, and the warming continued for a short time.   By this means the pulp was bleached to a completely white substance resembling paper-maker's "half-stuff."

The making of pulp from wood was rather difficult, because the shavings which were used as a starting point had to be ground up to some extent in a coffee mill, before treatment with caustic soda.   This treatment had to be repeated several times, as had also the intermediate hand-pulping, in order to get the material reduced to a sufficiently fine state for the next process.   The sulphite treatment and final bleaching were conducted in exactly the same manner as described under hemp.

THE QUANTITATIVE ESTIMATION OF FIBRES.—For the purpose of counting and thus estimating the proportion of fibres present, the low power (100 diam.) is quite sufficient. In the paper by Spence and J. M. Krauss, previously cited, a method of counting fibres is elaborated. This method depends on counting the number of diameters and fractions of a diameter, represented by each of the fibres under examination. The diameter taken as a unit is the diameter of a field examined under the microscope. Spence and Krauss deal mainly with woody fibres of various kinds and with rag. They find that equal weights of wood and rag, when mixed and examined under the microscope by their method, do not give equal numbers of diameters, and this they attribute to the fact that equal lengths of fibres do not represent equal weights; in order, therefore, to make correct estimations it is necessary to elaborate a correction which will convert the count expressed in diameters into weights. In the present work the object was to estimate hemp in the presence of wood. To do this, various synthetic mixtures were made up containing different proportions of hemp and wood. Three slides were made from each mixture, and the number of diameters of hemp and wood determined in about twenty fields, taken from each slide. The average of the whole was taken to represent the proportions of the two fibres present. When this was done, it was found that it was unnecessary to introduce any correction, such as that described by Spence and Krauss, because the results obtained by the diameters were sufficiently near the known proportions by weight. Sometimes the proportion of hemp was lower than the truth, and at other times it was higher, to about the same extent, and therefore no advantage could be obtained by introducing the correction for the relationship between diameter and weight. The following table shows the results obtained with synthetic mixtures of hemp and wood.

TABLE.

Quantitative Estimation of the Percentage of Hemp present in Mixtures of Hemp and Wood Pulp.

Taken Per cent.	Found Per cent.	Percentage errors
50 Hemp.	50·9	+1·8
33·3	29	−13
33·3	37·7	+13
80	80·3	+ ·4
25	30	+20
5	16	+60
10	9·3	− 7

It will be seen that when the percentage of hemp is fairly high, say, above 10 per cent., the results are sufficiently good for practical purposes. The figures shown under percentage errors may appear at first, high, but if the significance of the percentage error is realised, it will be seen that the accuracy of this method is probably rather better than that usually claimed by analysts experienced in paper analysis. Generally speaking, the claim is accuracy within about 5 per cent. This 5 per cent., of course, is not percentage error, and is, for that reason, rather

vague. The high percentage error shown in the table when only 5 per cent. of hemp is present is due to the enormous number of wood fibres to be counted. This naturally introduces cumulative errors. The accuracy of the method was also confirmed by examining a paper containing hemp and wood, the composition of which was unknown to the author. The results were found to correspond almost exactly with the composition as afterwards stated by the makers. The detailed method of carrying out the estimation of hemp is as follows:

METHOD.—Half a grm. of dry paper is weighed out and boiled with 100 c.c. of 10 per cent. sodium hydroxide to remove sizing materials. The paper is then pulped in a mortar until most of the paper structure has disappeared, after which the pulp is transferred to a cylindrical glass vessel (A) 5 in. high by 3½ in. in diameter, and thoroughly pulped by means of a hand egg-switch. When the pulp is thoroughly disintegrated it is transferred to a Winchester quart bottle, which is filled up with water and shaken thoroughly. The resulting mixture contains 0·02 per cent. of pulp, which is the concentration recommended by Spence and Krauss. A cylindrical vessel (B), about 6 in. high and 2 in. in diameter, is filled with this mixture, care being taken that the pulp is completely suspended in the water when the mixture is being poured out from the Winchester quart bottle. The quantity of pulp in the cylindrical vessel is now collected on a Gooch crucible fitted with a small piece of filter paper, and, after washing, the pulp is carefully separated from the filter paper and transferred to a test tube. It is now stained by Cross and Bevan's differential method, malachite green and Congo red being used, in the following manner:—A small quantity of a 0·5 per cent. solution of malachite green containing a little acetic acid is added to the test tube, and the mixture boiled for a few minutes. The pulp is again filtered off in a Gooch crucible under suction and thoroughly washed. It is next transferred to another test tube, stained with a small quantity of a 0·5 per cent. solution of Congo red, containing a little sodium carbonate, and filtered as before. The pulp so stained is transferred to the glass vessel (A), and the necessary amount of water added to bring it back to a concentration of 0·02 per cent. This is best done by filling the glass vessel (B) with water and adding it to (A).

The pulp is now brought into complete suspension by pulping it with a hand egg-switch, and the contents of vessel (A) are added to vessel (B). A microscopic teasing needle is taken and the pulp thoroughly stirred up with it. When the mixture has been made to rotate fairly quickly by stirring, the needle is held stationary near the side of the glass for a few minutes; the pulp will now be found to have twined itself round the needle, and a good average sample is obtained simply by withdrawing the needle from the mixture. Three micro-cover glasses, ¾ in. square, are taken, a small portion of the mixture is placed upon each, and very carefully teased out, so that individual fibres are subsequently seen under the microscope. The cover glasses are dried by pressure with a small piece of filter paper. A little alcohol is added to each, and the excess again removed by means of filter paper. A few drops of Canada balsam are placed on a micro-slide, and

one of the cover slips placed in position on the top of the Canada balsam in the usual way.   The excess of Canada balsam is removed by means of a little benzene.

The slide so prepared is placed on the stage of the microscope.   The Nicol prism is put into position, and an objective eye piece and tube length are so chosen as to give a magnification of 100 diams.   The polariser Nicol prism is fixed to the under side of the sub-stage condenser.   The slide is now examined both by ordinary and polarised light, the polariser Nicol prism being rotated in such a manner as to give either polarised or ordinary light as required.

The examination of the slide is begun on the top left hand corner, and successive fields are examined down the left hand side of the slide.   The slide is then moved so that practically the centre of it comes under the objective, and fields are examined right up the middle of the slide.   It is then moved to the right hand corner, and fields examined right down the right hand side of the slide.   The proportions of the fibres to be estimated are expressed in diameters and fractions of diameters of the field.   The total number of diameters of each fibre counted in the three slides is averaged, and the proportions of the fibres present calculated to percentages in the usual way.   As an example:—Suppose the total diameters of wood fibres to be 92·1, and those of the hemp to be 18·6.   The total number of diameters will be 110·7.   Hence, 110·7 diameters contain 18·6 diameters of hemp. One hundred parts will therefore contain:

$$\frac{18 \cdot 6 \times 100}{110 \cdot 7} = 16 \cdot 8 \text{ per cent.}$$

The author desires to express his thanks to Messrs. Eley Bros. for permission to publish the results given in this paper.

<div align="center">DISCUSSION.</div>

Mr. V. COFMAN asked whether the author could explain the reason for the difference in the appearance of the specimens when seen by polarised light, and whether, if the specimens had not been treated with the chemical reagents referred to, the appearance by polarised light would have been the same.

Mr. A. CHASTON CHAPMAN pointed out that monochromatic and ultra-violet light had been found capable of revealing differences in structures in the case of yeast and other organisms, and suggested that possibly the same methods of illumination might bring out differences in such fibres as those with which the authors had dealt.   He also wondered whether the readiness with which certain easily reducible metals could be deposited on the fibres could be made use of in ascertaining their origin.   He did not remember having seen any account of work on these lines, although the method had been usefully employed in other directions.

Mr. R. G. PELLY enquired whether the author's remarks applied only to true hemp (*Cannabis* species), or whether other kinds of hemp (such as Manilla and sisal hemp) were also referred to.   He also asked how the fibre had been pulped; whether a model paper beater had been used for the purpose, as beating might have some effect on the microscopic appearance of the fibres.

Mr. DICKSON, replying to the first speaker, said he was unable to explain why hemp, or any other fibre, behaved as it did under polarised light.   He was interested in the remarks on the possible effect of chemical treatment on the microscopic appearance of the fibre; in his experience the more one bleached the fibre the more apparent were the characteristic markings.   He had not tried the application of monochromatic light.   He was interested in the suggestion of the deposition of metals on fibre, which would doubtless be a fruitful field of research hitherto not explored.   As regards different kinds of hemp: he had examined a few different kinds—sunn hemp and ordinary Italian hemp; these were microscopically similar.   Manilla hemp, on the other hand, was different, but he had not studied it from the quantitative point of view.

Notes.

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

THE EXAMINATION OF FIREARMS AND PROJECTILES.

THE Editor has received the following expert notes and criticisms on Mr. Lucas's paper (ANALYST, 1923, 203) on this subject:

"The steel-capped bullets mentioned by Mr. Lucas were once used in the Swiss army, but have been replaced by one of most up-to-date design.

"In an endeavour to bring certain American and English express rifles up to date, a low pressure smokeless cartridge has been introduced to take the place of that for which they were originally designed, firing a lead bullet and a charge of black powder. In these cartridges the bullet is either completely or partially enveloped. Want of this knowledge might, perhaps, lead an investigator astray.

" 'Bonax' is not recognised as a brand of powder, but as a grade of shot gun cartridge made for many years by Kynochs (now incorporated in Nobel's Industries, Ltd.). It used to be loaded with a smokeless powder of the 33 grain class selected by the makers. This powder can safely be placed in the same general category as the others mentioned.

"Powders used in the filling of shot gun cartridges may be divided into certain classes, exclusive of the old-fashioned black powder, '42 grain,' '33 grain,' '30 grain,' and 'Concentrated.'

"The titles of the first three have a certain significance, meaning, as they do, that these represent the weights of the ordinary 12-gauge load, occupying the same bulk as the old standard charge of 3 drams of black powder. This was for the convenience of volume loading. 'Concentrated' powders are of the Ballislite order, with small bulk, and are loaded into a special type of cartridge case.

"Marshall's small *Dictionary of Explosives* (Churchill, 1920, price 15s.) will be found useful for reference in connection with powders.

"The statement about the smaller calibre of rifle bullets needs some modification. Modern rifle bullets are engraved and are not simply expanded to fill grooves under the influence of gas pressure, and the same remark also applies to revolver bullets. For example, the diameter of the ·303 bullet may be as much as ·009″ above that of the bore. The ·455″ unfired revolver bullet may be as much as ·014″ above that of the bore. Much useful evidence can be obtained from a sulphur cast, and the measurements, if taken fairly soon after casting, are very accurate. By filling the cap chamber of an old cartridge with wax a record of the striker imprint may be secured, but it will differ from that obtained from the cap of a fired cartridge, the form of which will be influenced by the internal pressure.

"With regard to the medium for receiving the bullet in experimental firing, it should be realised that certain high velocity bullets fly to pieces if fired into water. Dry sawdust will be found as suitable a medium as any. (See also Mann's experiments in *Bullets' Flight from Powder to Target.*)

"Drop shot is known by numbered sizes, the larger, moulded, shot by lettered sizes, but the number of pellets to the ounce of the former varies slightly with different makes. Nos. 5 and 6, the most common sizes for game, contain respectively 218 and 270 per ounce.

"There is obviously a typographical error on p. 206, paragraph 6, lines 5 and 6, which should state that 'British Army bullets, Marks VI. and VII. for example, are being hardened by the addition of 2 per cent. of antimony.'

"A caution must be given against placing too high a value upon the proportion of antimony as evidence of the identity of bullets in forensic cases. The amount of antimony may vary to quite an appreciable extent, owing to its falling out of solution, unless the maker takes precautions to prevent this. For the same reason home-cast bullets may show enormous variations in composition.

"Finally, it may be mentioned that revolver cartridges have been used in automatic pistols of the same calibre by removing a portion of the projecting rim, thus enabling the magazine to function."

A FORMULA FOR THE DETERMINATION OF THE NORMALITY OF A SOLUTION OF SULPHURIC ACID FROM ITS SPECIFIC GRAVITY.

THE published tables of Worden and Motion (*J. Soc. Chem. Ind.*, 1905, **26**, 178) give the number of grms. of pure sulphuric acid in 100 grms. of a dilute solution of that acid, whereas for analytical work it is necessary to know the number of grms. of pure acid in 100 c.c. of the solution.

From Worden and Motion's paper we find that acid of sp. gr. 1·0322 at 15·6° C., compared with water at the same temperature, contains 4·75 grms. of pure acid in 100 grms. of the solution, and that the change in the per cent. by weight is 0·015 for each increase of 0·0001 in the specific gravity.

It follows from this that, if the sp. gr. of a sample of acid is $1·0322+x$, the percentage of acid by weight is $4·75+0·015x/0·0001 =4·75+150x$; 100 c.c. of acid of sp. gr. $(1·0322+x)$ weigh $99·8 (1·0322+x)$ grms., and contain $99·8(1·0322+x)$ $(4·75+150x)/100$ grms. of pure acid. This amounts to $4·89315+159 ·26x+147x^2$. Now, since 100 c.c. of N sulphuric acid contain 4·9 grms. of pure acid, the factor will be obtained by dividing the above expression by 4·9, and we have

$$\text{Factor} =0·9986+32·5x+30x^2.$$

Or, if S is the observed sp. gr.,

$$F =0·9986+32·5(S -1·0322)+30(S -1·0322)^2.$$

If this expression is put equal to unity, then S is the sp. gr. of N sulphuric acid, which is thus found to be 1·03224.

If we use this value instead of 1·0322, the formula becomes

$$F =1+32·5(S -1·03224)+30(S -1·03224)^2;$$

the third term is negligible if the expression in brackets does not exceed 0·001.

C. C. ROBERTS.

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 interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

METROPOLITAN BOROUGH OF STEPNEY.
ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1922.

DURING the year, 1458 samples were analysed, of which 1417 (927 formal and 490 informal) were taken under the Food and Drugs Acts. The number of adulterated samples was 78 or 5·5 per cent.

MILK.—Twenty-six of the 838 samples of milk examined were adulterated. The average composition of all the samples was: Total solids, 12·40; solids-not-fat, 8·71; and fat, 3·69 per cent.

SPONGE CAKES.—Five of ten samples examined contained boric acid in amounts ranging from 15 to 28 grains per lb.

WHISKEY.—In most of the licensed houses in the borough a notice is exhibited that all spirits are sold as diluted spirits. It is suggested that such notices should state that they are posted to legalise the sale of spirits below the standard strength and should state the actual strength of the spirits sold. An informal sample contained 23 per cent. of excess water, and, on a subsequent visit by the inspector, a notice was displayed.

PRESCRIPTIONS UNDER THE NATIONAL HEALTH INSURANCE ACT.—Of 35 samples taken, 15 (=42·9 per cent.) were defective. Six samples of Mist. Sod. Sal. showed discrepancies in the amounts of sodium salicylate, ranging from a deficiency of 27 per cent. to an excess of 62 per cent. The vendor of the last-mentioned sample was fined £12 and £3 3s. costs.

LIME WATER.—Seven of 14 samples were adulterated, 5 being deficient in lime to the extent of 43 to 67 per cent., and 2 containing 2 parts of lead per million cf. ANALYST, 1923, 48, 116).

CANNED MEATS AND FISH.—Seventeen samples were examined. Six tins of salmon contained from 0·15 to 0·77 grain per lb. of metallic tin, and six of sardine paste from 1·15 to 2·06 grains. A tin of mutton essence (canned 1917) contained 4·7 grains; mutton broth (canned 1918), 0·2 grain; and essence of chicken (1918), 2·3 grains of tin. When a representative sample contained more than 2 grains of tin per lb. the batch was condemned.

<div align="right">H. HAWLEY.</div>

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.

DEFICIENCY OF QUININE SULPHATE IN A PRESCRIPTION.

ON May 30, an adjourned summons brought by the Hampstead Borough Council against R. J. G. Armatage, was concluded. The Government Analyst's report showed a deficiency of 6·5 per cent. of quinine sulphate instead of the 11·1 per cent. alleged by the Borough Analyst.

Dr. Scrase, Medical Officer of Health for Hampstead, stated that he regarded the deficiency in either certificate as a grave error.

Sir W. H. Willcox said that even a good sample of quinine sulphate would not be of 100 per cent. purity. He recognised and acquiesced in the practice of weighing the quinine sulphate, putting the proper quantity into an ordinary dispensing bottle, and filling the bottle with diluent. It was what 99 out of a hundred doctors in private practice did. In his opinion the certificate given by the Public Analyst was no evidence that the patient did not get 3 grains of quinine sulphate in each dose. The witness demonstrated the great difference in the limits of accuracy possible with a chemical balance, such as an analyst would use, and the ordinary dispensing scales, the latter being only correct within ¼ of a grain. He also showed the difference produced by surface tension when measuring liquids. He agreed that it was necessary to have the dose as correct as possible, but taking a common sense view, the deficiency alleged in this case (6·5 per cent.), or that in a second case (8·8 per cent.), were within the limits of permissible error.

In cross-examination, the witness stated that he would be very surprised to hear that 75 per cent. of the prescriptions dispensed at Hampstead had been absolutely accurate, and would find it hard to believe.

The Chairman of the Bench said that he proposed to give the defendant the benefit of the doubt and to dismiss the case.

TEST CASE TO SECURE A STANDARD FOR CREAM CHEESE.

Messrs. Welford & Co. were summoned, at the instance of the Holborn Borough Council, at the Bow Street Police Court, on April 30th, for the sale of cream cheese not of the nature and substance demanded by the purchaser.

It was stated, on behalf of the Borough Council, that a small cream cheese was purchased for 4½d., and that, on analysis, it was found to contain only 11·60 per cent. of fat. Proceedings had been taken because the Council thought it desirable that a standard should be fixed for cheese of this description. The Ministry of Agriculture had been approached on the subject, and it was thought that a prosecution might help to make them take action in the matter.

Mr. J. Keir Colwell, Public Analyst for Holborn, expressed the opinion that cream cheese should contain at least 20 per cent. of fat, and that he would expect to find 50 or 60 per cent. in a whole cream cheese. The sample in question could not be called "cream cheese" at all; he would describe it as "water cheese."

Mr. A. Todd, Professor of Dairying, University College, Reading, stated that, in his opinion, cream cheese should contain at least 50 per cent. of fat. This particular cheese was probably made from separated milk, and it would have a very much lower nutrient value than ordinary hard cheese.

Mr. W. T. Ricketts, for the defence, called evidence to show that the cheese was not sold as cream cheese, but as a " Bondon." According to one witness, none of the soft fancy cheeses stocked at this shop was ever described as " cream cheese." Full cream cheese could not be sold at the price charged.

At the adjourned hearing, on May 7th, an expert connected with the industry gave evidence to the effect that it was not possible to make cheese from cream. The term "cream" was applied to cheese in the same way as it was applied to "salad cream," "face cream," and so on. Almost any sort of soft cheese was loosely called "cream cheese." "Bondons" such as the cheese in question, were frequently called "cream cheese." They were usually made from partly skimmed milk or new milk. It was absurd to describe this particular "Bondon" as being made of separated milk. In that case there would have been, not 11·60 per cent. of fat, but only from 1·0 to 3·0 per cent.

The Magistrate (Mr. Graham Campbell), giving judgment on June 5th, said that as no regulations had been made under Sec. 4 of the Sale of Food and Drugs Act, 1899, it was necessary for him to make his own standard in accordance with the evidence before him. He could not accept the view of witnesses for the defence that when the public ask for a cream cheese all they want is a soft cheese such as a "Bondon" or a "St. Ivel" cheese. This was not in accordance with the evidence of some of the principal witnesses for the defence. When a complaint was made under Sec. 6 of the Act it was proper to take into consideration the price paid by the purchaser, and if one found that the purchaser was paying a price known to be the price of a commodity of higher quality than the commodity which was being supplied to him, one might infer that he was getting something not of the quality demanded. A "St. Ivel" cheese, which contained 27 per cent. of fat and weighed 6 ozs., was sold for 8½d., and a "Bondon" cheese, weighing 3 ozs. and containing 11 to 12 per cent. of fat, was sold for 4½d., so that the purchaser of

a cheese containing only 11 to 12 per cent. of fat was paying about as much as he would have to pay for the same quantity of a cheese with 27 per cent. of fat. Bearing in mind the fact that the word "quality" in Section 6, meant something more than a trade description, such as Bath bun, Scotch whiskey, or Irish whiskey, he thought it impossible to say that the article sold in this case was of the nature, substance and quality demanded. He did not consider it within his province to lay down any fixed standard of fat for cream cheese. It was sufficient for his purpose to say that a soft cheese containing 11 to 12 per cent. of fat could not properly be said to be of the nature, substance and quality of cream cheese. He was also of opinion that if a person paid the same price for a soft cheese containing 11 to 12 per cent. of fat as he did for a cheese containing 27 per cent. of fat, or if he got a cheese containing very much less fat than he had a right to expect in a cheese described as cream cheese, it was a sale to the prejudice of the purchaser.

A fine of £5 5s. and £15 15s. costs was imposed.

Parliamentary Notes.

HOUSE OF COMMONS.

July 4.

SKIMMED DRIED MILKS.—Replying to Mr. Hurd, the Minister of Health said that draft regulations for the proper labelling of skimmed dried milks had been prepared, and that they were being forwarded to other departments concerned as a preliminary to discussion. So far as he was aware, it would not be necessary to consult other countries in the matter.

PASTEURISED MILK.—Mr. Adams asked the Minister of Health whether he was aware that it was now possible, owing to modifications of previous orders under the Milk (Special Designations) Order, 1923, for milk which had been subjected to repeated heating processes to be sold to the public; and if so, whether he would take steps to prevent the retailing of such milk, or to have its exact nature indicated.

Mr. Neville Chamberlain replied that, under the Milk (Special Designations) Order, 1923, it was expressly provided that milk sold as "Pasteurised" milk should not be heated more than once.

He was advised that the danger to the public health from the sale of re-heated milk was not sufficient to justify the issue of special regulations which might, under the present conditions, lead to a restriction of the supply of milk.

Food Preservatives Committee.

THE Minister of Health has appointed a Committee consisting of the following : Sir H. C. Monro (Chairman), Professor W. E. Dixon, Sir A. D. Hall, Dr. J. M. Hamill, Mr. O. Hehner, Professor F. G. Hopkins, Dr. G. R. Leighton, Dr. A. P. Luff, Dr. C. Porter, and Mr. G. Stubbs, to inquire into the use of preservatives and colouring matters in food and to report :—(1) Whether the use of such materials or any of them for the preservation and colouring of food is injurious to health, and, if so, in what quantities does their use become injurious ;

(2) Whether it should be required that the presence of such materials and the quantities present in food offered or exposed for sale should be declared.

The Secretary of the Committee is Mr. A. M. Legge, of the Ministry of Health, Whitehall, S.W., to whom all communications should be addressed.

MINISTRY OF HEALTH,
    WHITEHALL, S.W. 1, 7th July, 1923.

Local Government and Other Officers' Superannuation Act.

THE Publication Committee wish to call attention to the fact that a very large number of local authorities are now considering, with a view to its adoption, the recently passed " Local Government and other Officers' Superannuation Act, 1922." Public Analysts who wish to be entitled to the benefits of that Act are therefore advised to take the necessary steps to see that the office of Public Analyst is included amongst those posts which are designated as established posts for the purposes of the Act*   EDITOR.

* Copies of the Act, price 6d. net, may be obtained from H.M. Stationery Office, Imperial House, Kingsway, London, W.C. 2 ; 37, Peter Street, Manchester ; 1, St. Andrew's Crescent, Cardiff ; or 23, Forth Street, Edinburgh.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Heat Coagulation of Milk. A. Leighton and C. S. Mudge. (*J. Biol. Chem.*, 1923, **56**, 53–73.)—On heating skim milk, the temperature of which is recorded by a delicate thermo-couple, the coagulation point coincides with an endothermic reaction, owing to which the temperature falls from 0·05 to 0·10° C. The authors have experimentally studied this phenomenon in connection with the stability of evaporated and condensed milks, and show that the absorption of heat is probably due to the precipitation of the calcium and magnesium combined with the proteins as citrates and phosphates. The thickening of condensed milk upon storage in the usual tins has been erroneously attributed to bacterial action, but it is shown that it is entirely due to chemical and physical actions. By heating milk in an oil bath, at such a temperature that the milk coagulates before reaching the temperature of the bath, indications are given of the relative stability of different samples towards heat. The period during which a milk remains un-thickened after evaporation and on storage is dependent upon the temperature and time of forewarming, the amount and time of adding cane sugar, and the temperature of storage.   T. J. W.

Iodimetric Estimation of Aldoses. I. M. Kolthoff. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1923, **45**, 131–141.)—Systematic investigation of the conditions under which the aldoses are oxidised quantitatively to the corresponding carboxylic acids yields the following results:—The iodimetric estimation of aldoses by means of hypoiodite may be carried out in two ways, the solution, after addition of iodine solution, being rendered alkaline by means of either sodium hydroxide or sodium carbonate solution. In the former case, the neutral sugar solution is treated with at least double the theoretical amount of iodine solution and then, with shaking, with at most a similar excess of sodium hydroxide solution; after the lapse of five to ten minutes (the latter time for lactose), the liquid is acidified and titrated with thiosulphate solution. When the carbonate method is employed, the liquid is treated with double the theoretical quantity of iodine solution, and then with 15 c.c. of 2 N-sodium carbonate solution; after twenty to thirty minutes, the solution is acidified by addition of 10 c.c. of 4 N-sulphuric or hydrochloric acid and titrated with thiosulphate.

If non-aldoses are present, the amount of iodine with which these combine must be determined under the experimental conditions employed. When dextrose in invert sugar is estimated, the result must be diminished by 1 per cent. to correct for the influence of the lævulose. Sucrose in quantities up to 2 grms. does not affect the results obtained with the use of 0·09 grm. of dextrose, but in presence of 3 grms. of sucrose the result obtained is 1·1 per cent. too high. For estimating lactose in presence of a large proportion of sucrose the sodium carbonate method is preferable to the sodium hydroxide method.   T. H. P.

Application of the Iodimetric Estimation of Aldoses to the Analysis of Mixtures containing Carbohydrates. I. M. Kolthoff. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1923, **45**, 141–147.)—The methods previously described (preceding Abstract) may be applied to the following estimations.

Lactose in Milk.—To 5 c.c. of the whey, prepared as described by Carrez (*Codex alimentarius*), are added 25 c.c. of 0·1 N iodine solution and 15 c.c. of 2N sodium carbonate solution, the liquid being acidified after 25 minutes with 10 c.c. of 4N hydrochloric or sulphuric acid and titrated with 0·1N thiosulphate solution: 1 c.c. of 0·1N iodine solution corresponds with 0·018 grm. of lactose.

Lævulose in Presence of Dextrose.—To a suitable quantity of the solution is added sufficient iodine to oxidise the dextrose, together with sodium hydroxide. After 5 minutes, the liquid is rendered just acid with hydrochloric acid, and the excess of iodine removed by addition, first, of a 10 per cent. solution and, when the liquid has become pale yellow, of a 1 per cent. solution, of sodium sulphite. After being made neutral to methyl orange, the liquid is made up to 100 c.c., and the lævulose in 25 c.c. estimated by Schoorl's method (1899).

Dextrose, Lævulose and Sucrose.—The dextrose is estimated iodimetrically, and then either the dextrose and lævulose together estimated by means of Fehling solution, or the lævulose alone estimated as in the preceding paragraph. For each 0·1 grm. of lævulose present in the amount of the sugar taken for the iodimetric

test the number of c.c. of $0·1N$ iodine solution used is diminished by $0·1$. To estimate the sucrose, a solution of the substance in 50 c.c. of $0·02 N$ hydrochloric acid is heated for 30 minutes in a boiling water-bath, and then neutralised towards methyl orange by means of $0·1 N$ sodium hydroxide solution, and made up to a definite volume. The dextrose now present is estimated iodimetrically, again with correction for the lævulose, and the sucrose calculated.

Dextrose, Lævulose, Sucrose and Dextrin (Starch Syrup).—The three sugars are estimated as just described. To hydrolyse the dextrin, so much water or hydrochloric acid is added to a suitable quantity of the substance or solution that, for a volume of 75 c.c. the concentration of the acid is normal. The flask containing the liquid, covered with a small funnel, is heated for an hour in a boiling water-bath, and then rendered almost neutral to methyl orange by addition of 50 per cent. alkali hydroxide solution, and made up to a definite volume. If the original solution contained an appreciable amount of lævulose or sucrose, the liquid is now shaken with just sufficient adsorbent charcoal to give a colourless or almost colourless filtrate. The dextrose content is again estimated by the hypoiodite method, and the dextrin then calculated. T. H. P.

Ceylon Arrack. C. T. Symons and W. N. Rae. (*J. Soc. Chem. Ind.*, 1923, **42**, 252–254 T.)—Analyses of fifteen samples of arrack of various ages, three of which were produced in a government distillery and the remainder in private distilleries, showed the following extreme limits: Colour ranged from dark brown to colourless; alcohol, 19·8 to 26·6 u.p.; extract, 18·6 to 384; acidity (as acetic) (fixed) 1 to 19, (volatile) 43 to 406; esters (as ethyl acetate), 67 to 405; aldehydes (as acetaldehyde), 9·2 to 88·8; furfural, 0·5 to 3·5; higher alcohols (as amyl alcohol), 121 to 460; and copper (derived from the copper condenser worms), nil to 6·1 mgrms. per 100 c.c. of absolute alcohol. Arrack obtained by illicit distillation is known as "pot arrack," and is distilled with two clay pots connected by a bamboo; thus the product is entirely free from copper. Analyses of three illicit samples which were colourless but cloudy, owing to the presence of suspended matter, showed the following limits: Alcohol, 29·5 to 39·4 u.p.; extract, 494 to 967; acidity (fixed) 1 to 3, (volatile) 179 to 430; esters, 119 to 324; aldehydes 24·9 to 78·8; furfural, 0·29 to 0·51; and higher alcohols 157 to 222 mgrms. per 100 c.c. of absolute alcohol. T. J. W.

Effect of Fish Meal upon the Fat of Hogs. J. B. Martin. (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 498–501.)—The fat of hogs fed upon a diet containing from 11 to 14 per cent. of fish meal was found to be free from fishy odour and flavour and yielded physical and ordinary chemical characteristics identical with those given by normal fat. Examination of the fat for the presence of fish oils by the official method (*A.O.A.C.*, 1920, 256) yielded a small but definite precipitate of an insoluble bromine addition compound. The estimation of clupanodonic acid by treatment of the liberated fatty acids in ether and acetic acid solution with bromine gave 0·15 per cent. of octobromstearic acid, corresponding to 0·045 per cent. of clupanodonic acid. Bromination of the fatty acids immediately after

preparation yielded a product containing 68·8 and 67·9 per cent. of bromine, the theoretical value for octobromstearic acid being 69·84 per cent.   T. J. W.

Oxygen and Perforations in Canned Fruits. E. F. Kohman. (*J. Ind. Eng. Chem.*, 1923, **15**, 527–528.)—In the case of tinned apples any oxygen left in the tin disappears within a few days when plain tins are used, but it disappears slowly when the fruit is preserved in enamelled tins. This indicates that the disappearance of the oxygen is due to its action on the tin plate rather than to combination with the apples, and may explain the fact that enamelled tins perforate more rapidly than do plain tins. The length of time that the oxygen remains in enamelled tins appears to be proportional to the completeness with which the tin plate is protected by the enamel. The most efficiently enamelled tins would therefore not only contain oxygen for a greater length of time, but would also have it in greater concentration. Moreover, all the oxygen would be available for the small exposed areas of the tin plate. Oxygen obeys the law of mass action in causing perforations rather than acting as a catalyst.   W. P. S.

Use of Artificial Resins for Polishing Coffee. J. Bordas. (*Ann. Falsificat.*, 1923, **16**, 221–224.)—Artificial resins derived from coumarone are neither poisonous nor hygroscopic, but their use for polishing coffee results in the formation, on the berry, of a layer of impermeable varnish which prevents loss of moisture by evaporation, even from coffee which has been steamed while hot. These resins are neutral, and unsaponifiable, and dissolve in acetone or petroleum spirit, and, to a slight extent, in alcohol, but are insoluble in alkalis. Their melting points range from 80° to 150° C. For their detection the coffee is treated with pure petroleum spirit (benzine), the solution evaporated to dryness, and the residue saponified. The non-saponified residue is dissolved in about 5 c.c. of pure petroleum spirit, and the solution shaken with an equal volume of concentrated sulphuric acid; the presence of coumarone resin is indicated by the assumption, after one or two minutes, of a reddish-brown coloration by the acid. Vaseline oil, the use of which is permitted for polishing coffee, is also soluble in petroleum spirit, but gives no coloration with sulphuric acid.   T. H. P.

New Method for Estimating Theobromine in Cocoa. T. Ugarte. (*J. Pharm. Chim.*, 1923, **27**, 420–423.)—The method applied to the estimation of theobromine in coffee, tea, etc. (*J. Pharm. Chim.*, 1921, **24**, 387) is adapted to cocoa in such a way that the whole operation can be completed in about 2½ hours, and a very pure product obtained. Half a grm. of powdered cocoa is carefully weighed into a 500 c.c. Kjeldahl flask and gently heated so that no white fumes escape from the neck of the flask. After complete carbonisation, 10 c.c. of distilled water are added to the cooled mass, and the whole boiled with frequent shaking. The liquid is then filtered into a crystallising dish 7 cm. diameter by 2 cm. deep, the treatment with distilled water repeated twice and the filtrates evaporated to dryness. Two portions of 5 c.c. of alcohol are added to the dry residue, the alcohol decanted, and any remaining alcohol evaporated on the water bath. Three c.c.

of distilled water and 11 drops of *N* ammonia solution are then added, and the whole mixed so that the residue is either dissolved or suspended in the liquid. Fifteen c.c. of chloroform are next added, and the whole stirred for 5 minutes in order to dissolve as much as possible of the theobromine. The mass is then transferred to a double filter paper (the inside one a weighed paper), and the dish and stirrer washed with three successive portions of chloroform. The water is retained by the papers, and the chloroform solution then evaporated to dryness. The white residue resulting is taken up with 5 c.c. of distilled water, heated (with stirring) for 3 minutes on a water bath, and the solution filtered through a weighed filter paper of 5 or 6 cm. diameter into a weighed watch glass, the dish being then washed out with two successive portions of 3 c.c. of distilled water, and the watch glass heated for 2 minutes on the water bath. The filtrates are then evaporated on a water bath, and the white micro-crystalline residue dried in the oven at 100–105° C. for 5 minutes. The increase in weight gives the amount of theobromine obtained. Eight samples of cocoa purchased at Buenos Ayres contained from 0·45 to 1·17 per cent. of theobromine, the cheaper varieties containing the smaller quantities. D. G. H.

New Source of Cantharidin. A. Viehoever and R. G. Capen. (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 489–492.)—The American blister beetle, *Macrobasis albida*, Say., found in abundance in Texas, Kansas and the neighbouring states, yields from 0·6 to 1 per cent. of free cantharidin, and from 4 to 5 per cent. of total cantharidin. The estimations were carried out by Dubois' method (*Amer. J. Pharm.*, 1920, **92**, 157) and the distribution of cantharidin in the insect was found to be very variable, the eggs containing large quantities, whilst a small amount was present in the heads and none in the wings. The optical properties and solubility of cantharidin in various solvents are given. T. J. W.

Saffron and its Adulterants. G. Pierlot. (*Ann. Falsificat.*, 1923, **16**, 215–221.)—Saffron is sold in two qualities: Ordinary saffron (*safran courant*), consisting of the three red stigmata joined to a single yellow style and known in certain pharmacopœias as *Crocus naturalis*; and cut saffron or Austrian saffron, composed of the red stigmata freed from the style and known also as *Crocus electus*. Adulteration of saffron with plant juices, sodium glyceroborate, or potassium nitrate is now rarely encountered, the usual method consisting in steeping saffron for a time in a solution of sugar or sodium sulphate and then allowing it to dry slowly in the air. Genuine saffron imparts to the flame the violet colour due to potassium or, in some cases, an orange, but never a yellow tint. Adulteration with sugar is indicated by an orange-yellow flame which obscures the violet potassium coloration. A suspected sample may be analysed as follows:— The saffron is dried at 95–100° C. for two hours, and, after powdering, for a further period of an hour; the dried powder is kept in a desiccator over sulphuric acid. Estimations are made, on this material, of: (1) The nitrogen. (2) The ash. (3) Reducing power, before and after inversion by acid. For this purpose, 2·5 grms. of the saffron are placed on a glass-wool plug in a tube about 30 mm. in

diameter and 15 cm. long, drawn out at one end, about 200 c.c. of water being allowed to fall, drop by drop, on to the saffron; the filtrate is made up to 250 c.c. and filtered, and the two reducing powers measured. (4) Sodium sulphate. This may be detected in the aqueous extract by addition of barium chloride, and may be estimated by evaporating this extract to dryness, incinerating the residue and estimating the sulphate in the ash. The percentage of nitrogen in ordinary saffron is 2·30, and that in cut saffron 2·40, and the difference of the actual amount from these figures serves to calculate the extent of adulteration. With genuine saffron the reducing power towards Fehling solution is slightly increased by inversion with acid, the amount of added sucrose being deduced by multiplying by 0·95 the difference between the reducing powers before and after inversion.

T. H. P.

Food Colourings. **F. W. Richardson.** (*J. Soc. Dyers and Colourists*, 1923, **39,** 148-149.)—The use of the following mineral pigments for colouring food is permissible in the United States:—Manganese brown, ultramarine blue, ultramarine violet, and iron oxide brown. Aniseed balls sold in this country have been found to contain as much as 2 per cent. of iron oxide. Of the coal tar dyes, those containing nitro and nitroso groups are more or less toxic, whether the group replaces a hydrogen atom in the nucleus or one in the hydroxyl group.

Yellow Dyes.—Aurantia (the ammonium or sodium salt of hexanitrodiphenylamine) and picric acid are poisonous, whilst naphthol yellow S, known also as acid yellow S, and citronine A (the sodium or potassium salt of dinitro-α-naphthol-β-monosulphonic acid) are not poisonous, since, in spite of two nitro groups, the presence of a sulphonic acid group causes neutralisation of the toxic action. Tartrazine or hydrazine yellow contains not only two sulphonic acid groups, but also a carboxyl group, the presence of which reduces toxicity. Curcumin S, also known as "sun yellow" (the sodium salt of azo-stilbene-disulphonic acid) is also non-toxic. Napthol yellow S and tartrazine are the chief food colourings now used—sometimes under the significant name of "egg yellow." Martius yellow (also named naphthol yellow), unlike its sulphonated derivative, naphthol yellow S, is poisonous.

Red Dyes.—The following red dyes are safe to use because of their high sulphonic acid content and their freedom from nitro and nitroso groups:—Naphthol red S (amaranth, fast red D, Bordeaux S), chloramine red B (benzo-scarlet BC), carmoisine (azorubine S, fast red C), ponceau 2R, fast scarlet BC, and rhodamine B. Eosine (tetrabromfluorescein) and erythrosine D and B (the sodium or potassium salt of tetraiodofluorescein, which contains up to 40 per cent. of iodine) are also non-toxic.

Blue, Violet and Green Dyes.—Xylene blue BS and gentian blue 6B (spirit-soluble blue) is a salt of triphenylrosaniline and triphenylpararosaniline. It is said to be physiologically inert, as are also blues derived from diphenylamine. Coupier's blue or nigrosine (spirit black or oil black) is a similar dye. Methyl violet 6B (Paris and benzyl violet) usually contains over 20 per cent. of zinc, as

does also Victoria green or new fast green 3B, but violets and greens such as malachite green, new green, fast green, ethyl green, emerald green, fast green J, and benzaldehyde green are made without zinc, and are regarded as harmless for food colouring.   In the United States the use of diamond green (sodium carboxy-phenolazo-*a*-naphthalene-azo-dioxynaphthalene   disulphonate)   and   fast   green (sodium tetramethyldiamino-triphenyl-carbinol-*m*-carboxylic acid) is permitted, as also is that of dinitroresorcinol (fast green O, dark green, chlorin, Russian green, fast myrtle, and Alsace green).

 Brown Dyes.—The only brown dye permitted by the U.S.A. authorities is Chrysamine R.   Brown, however, is only used for sweets, and the colour chosen is usually an iron oxide brown (*cf.* ANALYST, 1922, **47,** 438).

Biochemical, Bacteriological, etc.

Mode of Action of Vitamins. W. Cramer. (*Lancet,* 1923, **204,** 1046–1050.)—The effect of a diet free from vitamin *A* upon the rat is to produce profound atrophy of the villi of the small intestine and necrosis of the upper parts of many of the villi.   In addition, protozoa, mainly *Giardia intestinalis* (*Lamblia intestinalis*) are enabled to proliferate rapidly and to penetrate down between the villi, where normally they are never present, and the intestinal bacilli also appear to be present in larger numbers than normally.   In cases of vitamin *A* deficiency, the progressive atrophy of the intestinal mucous membrane leads to a continued and increasing invasion of the blood stream by intestinal bacteria which are being agglutinated by the blood platelets.   This results either in an excessive drain on the platelets, or more probably, in a direct atrophic change in the tissue or cells which form platelets.   When vitamin *A* is supplied again in abundance by giving cod-liver oil, the intestinal lesion heals over rapidly, the invasion of the blood stream by bacteria is arrested, the platelets rapidly increase in number, and the normal defences of the organism are enabled to deal with virulent bacteria. In the absence of vitamin *B* from the diet of the rat, the normal assimilation of food is impaired owing to the atrophy of the lymphoid tissue of the digestive tract, and this tissue recovers when the appropriate vitamin is administered after a previous deficiency.   There is also evidence that an organism recovers more rapidly from a lymphopenia induced by radiation when an abundant supply of vitamin *B* is administered.   The functional integrity of the digestive tract is thus dependent on the presence in the food of certain substances with specific drug-like actions, very much in the same way as the functional integrity of the uterus is dependent on a hormone produced by the ovary.   These accessory food substances may therefore be looked upon as "food hormones."   Two groups with different specific actions can at present be distinguished.   One of these (now called water-soluble vitamin *B*) has a specific stimulating action on lymphoid tissue.   The other group (now called the fat-soluble vitamin *A*) has a specific stimulating effect on the intestinal mucous membranes, and also directly or indirectly on the formation of blood platelets.

Vitamins and Light.—Rats kept in the dark since birth show a considerable reduction in the number of blood platelets. They exhibit no gross intestinal lesions, and their growth and appearance are normal when compared with rats kept in daylight. But when exposed to a deficiency of fat-soluble vitamin they develop the characteristic lesions (xerophthalmia, septic lymph glands) sooner than rats kept in daylight. Conversely, when rats are kept on a diet free from vitamin A the application of light delays the fall in the number of platelets; it also delays the onset of xerophthalmia and the general decline of the animal, although it cannot altogether prevent them. The apparently paradoxical fact that light can, to a certain extent, counteract a dietetic deficiency can thus be explained on morpho logical grounds as follows:—A deficiency of vitamin A produces a twofold lesion—a lesion in the intestinal mucosa and a diminution in the number of platelets. Light acts as a stimulus to the formation of platelets, and thus strengthens one of the defensive mechanisms against bacterial invasion from the intestines.
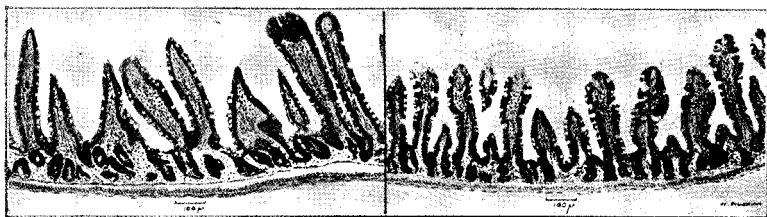
Fig. 1.

Small Intestine of Rat (longitudinal section). Fixed in formol solution. × 40.

Fig. 2.

Small Intestine of Rat (longitudinal section). Shows effect of vitamin underfeeding as compared with Fig. 1. × 40.

Fig. 3.

Small Intestine of Rat (longitudinal section). Kept on diet free from vitamin A for 5 weeks. × 40.

Fig. 4.

Small Intestine of Rat (longitudinal section). Kept on diet free from vitamin B for 4 weeks. × 40.

Insecticidal Principle of Pyrethrum Flowers. J. Chevalier and F. Mercier. (*Comptes rend.*, 1923, **176**, 1847–1848.)—The insecticidal action of *Chrysanthemum cinerarifolium* and allied species of plant is due, neither to an alkaloid nor a glucoside, but to an oleo-resin composed of a readily saponifiable ester, the liberated acid of which is also active, although to a less extent. This ester can be extracted from the flowers and from the whole plant by means of

cold alcohol, and can be separated from waxes, resins and other impurities by treatment with ether and petroleum spirit.   It is insoluble in water.   It is toxic to cold-blooded animals, much less toxic to warm-blooded animals, but is harmless to man.   Its action upon muscular tissue somewhat resembles that of veratrine, producing central paralysis.

Outbreak of Food Poisoning traced to Egg Salad.   C. E. A. Winslow, J. V. Hiscock, O. F. Rogers, and E. S. Robinson.   (*Amer. J. Hygiene*, 1923, **3**, 238–246.)—In November, 1922, an epidemic of acute gastro-intestinal intoxication, including 51 cases, occurred at Yale University.   The source of infection was traced to egg-salad, which had been prepared by a coloured cook.   A typical organism of the paratyphoid B group was isolated from the stools of several of the patients.   Although the organism could not be detected in the fæces or urine of the cook, there was some reason to suspect that he was a temporary carrier and the original source of infection.

Effect of *Gambusia affinis* on the *B. Coli* Index of Pollution of Water.   L. C. Havens and S. A. Dehler.   (*Amer. J. Hygiene*, 1923, **3**, 296–299.)—Reservoirs are frequently stocked with top minnows, especially *Gambusia affinis*, to prevent the breeding of mosquitoes.   Experiments have proved that the presence of these fish causes the immediate disappearance of *B. coli* from sewage-polluted water.   The normal intestinal flora of *Gambusia* in Alabama waters are *B. pyocyaneus*, and an unidentified aerobic, lactose-fermenting, spore-forming bacillus, but *B. coli* is not normally present.   The effect of *Gambusia* in causing the disappearance of *B. coli* from polluted waters is due to the inhibitory influence of *B. pyocyaneus*, and this experimental evidence indicates that the presence of considerable numbers of *Gambusia* may render the *B. coli* index an untrustworthy criterion of pollution.

Observations on the Growth of the Influenza Bacillus.   S. R. Damon.   (*Amer. J. Hygiene*, 1923, **3**, 247–251.)—It has not been found possible, under the experimental conditions described, to grow the influenza bacillus on heat-killed emulsions or water extracts of mucoid organisms—Friedländer's bacillus and *B. Pfeifferi*—or of *B. proteus*.   Nor has it been found that an egg medium containing the bodies of *B. phlei* will support continued growth of *B. influenzæ*.

In the author's opinion, there is no justification for including among the *vitamins* substances found in bacterial cultures, which apparently stimulate the growth of other micro organisms, as has been suggested by Thjötta (*J. Exper. Med.*, 1921, **33**, 763), Twort (*Lancet*, 1921, **201**, 5120), and Bottomley (*Proc. Roy. Soc.* [B], 1915–17, **89**, 481).   To claim that a growth-stimulating substance, found in cultures of *B. Friedländer*, *B. Pfeifferi*, *B. proteus*, *B. phlei*, or in aerobic soil organisms, is a member of a class of vitamins, would seem to be pure assertion, unless it has been subjected to the biological test.   A report on such a test will be made subsequently.

Rapid Enumeration of Micro-organisms in Milk. E. Pozzi-Escot. (*Ann. Chim. anal.*, 1923, **5**, 130–132.)—The U.S.A. method of counting the bacteria in milk by drying one c.c. of the milk spread over an area of 1 sq. cm., and then staining and counting the organisms in a small part of that area, is unsatisfactory on account of the inequality of the film and the enormous multiplying factor required to translate the number counted to the number per c.c. The method proposed is based on Wright's method for the determination of opsonic indexes, as follows:—A solution of fresh normal blood (1:10000) is prepared by adding one drop of blood to 50 c.c. of isotonic serum, a drop of this diluted solution is then mixed with great care in a slide with a drop of the milk and the mixture spread out, dried, freed from fat by washing in xylene for two or three minutes, and fixed by washing in strong alcohol. After fixing, the film is stained for half a minute with methylene or thionine blue, and the red blood corpuscles are partially de-colorised by dipping the slide several times in methyl alcohol. The film is ex-amined under an oil immersion objective, the number of red corpuscles (x) and of bacteria (y) in several fields are counted. Since, at this dilution of blood, there should be 500,000 red corpuscles per c.c., the relation $\dfrac{500,000 \times y}{x}$ gives the number of bacteria per c.c. in the milk. The method can be made still more accurate by using a pipette instead of drops for the measurement of the milk and the blood solution; there is a small error due to decolorisation of certain bacteria, but errors due to uneven distribution on the slide and the large multiplying factor are eliminated, and the results obtained are almost identical with those of plate culture methods which require at least 48 hours. H. E. C.

Estimation of Urea in Cows' Milk. Y. Morimoto. (*J. Biochem. Japan*, 1922, **69**; *Ann. Chim. anal.*, 1923, **5**, 153.)—Urea in urine or in milk is estimated by means of urease which may be obtained from the seeds of *Canavalia ensiformis* by extracting the powder with glycerin and water, then, after about three hours, acidifying with hydrochloric acid and filtering. In the case of urine, the estimation is carried out by diluting about 5 c.c. with 50 c.c. of water and adding 3 c.c. of the solution of urease and 1 c.c. of 3 per cent. solution of calcium caseinate to serve as indicator; after about three hours 40 c.c. of 0·1 N hydrochloric acid are added, and the excess of acid titrated back with sodium hydroxide solution, the pre cipitation of the casein indicating the end-point. In the case of milk, 10 c.c. are diluted with 40 c.c. of water, 3 c.c. of urease solution are added, and the estimation continued as above. Cows' milk usually contains 0·25 to 0·30 grm. of urea per litre and, for the first few weeks after calving, 0·75 grm. per litre. Goats' milk is richer in urea than that of the cow, the average being 0·80 grm. per litre. H. E. C.

Preparation of Standards for the Estimation of Creatine and Creatinine. G. Edgar. (*J. Biol. Chem.*, 1923, **56**, 1–6.)—The advantages and disadvantages of the various substances used as standards for the Folin colorimetric method

are discussed, and the preparation of pure salts from commercial creatine, now obtainable at a greatly reduced price, is described. *Creatinine zinc chloride*: The creatine is ground with an equal weight of anhydrous zinc chloride, and the mixture is heated, with constant stirring, until, at about 130° C., the viscous mass suddenly solidifies. After cooling, the solid is dissolved in 10 times its weight of boiling 25 per cent. acetic acid, and twice the volume of alcohol is added, the mixture then being allowed to cool. Creatinine zinc chloride crystallises out almost quantita- tively and in a high degree of purity. *Creatinine picrate*: Commercial creatine is dissolved in an excess of 22 per cent. hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in a little water and added to a slight excess of picric acid dissolved in boiling water or boiling alcohol. On cooling, the separated picrate is filtered off, washed with cold water, recrystallised once from boiling water and dried at 100° C. Samples prepared by this method melted within 0·5° of 205° C. (uncorrected), and were shown by other tests to be pure. Standard solutions were prepared from these salts (the zinc compound solution containing 1·602 grm. per litre and the picrate solution 1·5119 grm. per litre), and compared by the Folin method with a solution of the zinc compound prepared from pure creatinine and repeatedly recrystallised. The results obtained were identical, whether comparisons were made in various colorimeters or in Nessler glasses. Creatinine picrate is stable, both in the solid form and in solution, for long periods, and is not explosive, but is only slightly soluble in water. Creatinine zinc chloride in aqueous solution is gradually converted into creatine, but this may be prevented by the addition of acid to the solution.   T. J. W.

Quantitative Estimation of Phenols in Blood. N. W. Rakestraw. (*J. Biol. Chem.*, 1923, **56**, 109–119.)—The following method is a modification of one described by Folin and Denis (*J. Biol. Chem.*, 1915, **22**, 305; 1916, **26**, 507) in combination with the uric acid estimation of Morris and Macleod (ANALYST, 1922, **47**, 176). The sample of blood is laked by the addition of 7 volumes of water, and proteins are precipitated by treatment with 1 volume of 10 per cent. sodium tungstate solution and 1 volume of 3·26 per cent. sulphuric acid. After standing for some time, the mixture is filtered, and to 25 c.c. of the clear filtrate 1 c.c. each of 2·5 per cent. zinc chloride solution and 10 per cent. sodium carbonate solution are added, after which the liquid is well stirred, allowed to stand for 1 hour and centrifuged, the precipitate being reserved for the estimation of uric acid. To 10 c.c. of the clear solution 0·5 c.c. of Bell's diluted phenol reagent (ANALYST, 1922, **47**, 217) and 2 c.c. of 20 per cent. sodium carbonate solution are added, the mixture being stirred and allowed to stand at least 30 seconds, after which 1 c.c. of 5 per cent. sodium cyanide solution is added, and the container is immersed in a boiling-water bath for 1½ minutes, followed by cooling in running water for at least 3 minutes. The colour produced is compared with that of a standard phenol solution (containing 0·0025 to 0·003 mgrm. per c.c.), which has been subjected to the same treatment. The free phenols only are estimated by the above method, but the total (free+conjugated) quantity present may be evaluated by heating

10 c.c. of the clear solution, after centrifuging, with 0·25 c.c. of concentrated hydrochloric acid under a reflux condenser for 10 minutes and nearly neutralising the cooled solution with 0·5 c.c. of 20 per cent. sodium carbonate solution. Similar quantities of acid and alkali are added to the standard solution, which is not heated, the subsequent procedure being as detailed above. In estimations on blood to which known amounts of phenol were added the amounts recovered varied from 94 to 110 per cent. Since a resorcinol standard has been employed by previous workers, the empirical colour equivalents of this and other phenols have been estimated with the following results: 1 mgrm. phenol =0·911 mgrm. resorcinol; 1 mgrm. *p*-cresol =0·713 resorcinol; and 1 mgrm. *o*-cresol =0·77 mgrm. resorcinol. Experiments to investigate the optimum conditions of the method are described in detail. T. J. W.

Toxicological and Forensic

Detection of Formaldehyde in Organic Material. H. Lührig. (*Pharm. Zentralh.*, 1922, **63**, 597–602; *Chem. Abstr.*, 1923, **17**, 704.)—Experiments were made in connection with a toxicological case involving the possible ingestion of formalin, to ascertain the longest interval during which formaldehyde could be detected after its administration. It was found that, contrary to previously accepted views, a positive reaction could be obtained over a period of 29 days after administration in soup; in milk after 11 to 31 days; and in beans up to 8 days. After admixture with urine (old and fresh) it could be detected for 8 and 28 days respectively, for 39 days in a human stomach and contents, and for 27 days in a human small intestine and contents. In several of the tests the detection was possible only with the undiluted distillate.

Water Analysis.

Hydrogen Ion Concentration of Natural Waters (and of some Etching Reagents) in Relation to Action on Metals. W. R. G. Atkins. (*Trans. Faraday Soc.*, 1923, **18**, 310–315.)—The common idea that moorland waters are of considerable acidity is incorrect, unless they are derived directly from peat bogs. Dartmoor waters from peat bogs have an acidity equivalent to $P_H = 5\cdot0$ to $5\cdot5$, but springs and streams in the same locality, although containing carbon dioxide which brings the P_H value up to 6·9, become alkaline by aeration and then have $P_H = 8\cdot5$. Rain water shows an equilibrium between dissolved carbon dioxide and that in the air, and has $P_H =$ about 5·9; on storage in glass it becomes alkaline. Sea water (off the Cornish coast) has $P_H = 8\cdot14$ at 10° C., rising in spring and summer to 8·2 or 8·3 owing to photosynthetic action, or rising even to 9·7 in the presence of abundant algae. A metal is not appreciably dissolved by an acid, unless the hydrogen ion concentration suffices for the solution of its hydroxide. The range of precipitation of ferrous hydroxide extends from $P_H = 5\cdot1$ to $P_H = 7\cdot6$, whereas that of ferric hydroxide is $P_H = 3\cdot6$ to 6, so that the merest trace of acid suffices to dissolve iron. In the first stage ferrous hydroxide is produced, which is in turn oxidised by

dissolved oxygen to the ferric state and precipitated, with the reproduction of acid. Similar considerations apply to lead. The precipitation of ferrous iron is not complete even at $P_H = 7 \cdot 1$, but beyond $P_H = 6 \cdot 3$ there is practically complete immunity from action, as the carbon dioxide in solution as acid is vanishingly small. Attention is drawn to the possible utility as etching agents of buffer solutions and of acids of relatively low hydrogen ion concentrations, since it is possible to have such a P_H value as will result in the attack of one metal, whilst another is left intact. The effect of dilution being less in the case of weak acids or bases, their action remains more uniform at low concentrations than is the case with strong acids or bases. For example, a 10–15 per cent. solution of tartaric acid has $P_H = 1$, and is useful for etching an alloy of $1 \cdot 5$ per cent. antimony with tin.   H. E. C.

Phenol-Chlorine Water Pollution. New Reaction between Phenol and Chlorine. E. F. Kohman. (*J. Ind. Eng. Chem.*, 1923, **15**, 518.)—A town water supply, which had been purified by chlorination, had a distinctly unpleasant taste and odour, particularly when the water was heated. It was found that the water before treatment had been contaminated by the effluent from a coke plant, and it was possible that the odour and taste of the water were due to the presence of chlorophenols. Investigation showed that a solution of 1 part of phenol in 780 millions parts of water had a pronounced taste when chlorinated, and that the taste was quite different from the phenolic one observed when the concentration of the phenol was greater than 1 part per 50 millions. The ordinary chlorophenols could be tasted in a solution containing 1 part in 10 to 50 millions, but not in 100 millions, indicating that in the greater dilutions phenol and chlorine react other than in the usual way.   W. P. S.

Detection of Toxic Organic Combustion Products in Effluents. Ach. Gregoire. (*Bull. Soc. Chim.*, 1923, **32**, 230–232.)—Examination of the effluents from various works revealed the fact that waters containing organic combustion products, such as those coming from works with blast furnaces and coke ovens; from gas works, wood distillation, and creosoting works, and aluminium acetate factories, are by far the most toxic to fish. Such waters when treated with Fransen and Egger's reagent (200 grms. of mercuric chloride, 300 grms. of sodium acetate, and 80 grms. of sodium chloride per litre), and then boiled on a water bath for 2 hours, give precipitates of varying intensity according to the amount of such combustion products present. Waters from sugar refineries also give the reaction, but in them the reducing substances are readily oxidised, usually before reaching the river. In the case of sewer effluents, the reducing bodies are not found after distillation, and the reagent should always be applied to the distillate of the sample.   D. G. H.

Detection of Nitrites in Water. A. Zlataroff. (*Zeitsch. anal. Chem.*, 1923, **62**, 384–385.)—Ten c.c. of the water to be tested are well mixed with 1 to 2 c.c. of a $0 \cdot 002$ to $0 \cdot 003$ per cent. aqueous solution of neutral red; addition of a few c.c. of

dilute hydrochloric or sulphuric acid immediately produces an intense blue colour if nitrites are present. Iron, manganese and other metals occurring in natural waters do not interfere. W. R. S.

Estimation of Silica in Waters. F. Diénert and F. Wandenbulcke. (*Comptes rend.*, 1923, **176**, 1478–1480.)—The following method serves for the estimation of the colloidal, and also of the non-colloidal, silica in water. To 50 c.c. of the water or of a sodium silicate solution are added 2 c.c. of 10 per cent. ammonium molybdate solution and 4 drops of sulphuric acid (1:2). A yellow coloration develops during 10 minutes and then remains of constant depth for about 3 hours. By comparison of the colorations obtained with the water and with a standard sodium silicate solution the silica content of the water may be estimated with an accuracy of about 2 per cent. When numerous estimations have to be carried out, the matching may be made with an aqueous solution containing 0·0369 grm. of picric acid per litre, this having exactly the colour given by a solution containing 0·050 grm. of silica per litre. The maximum quantity of silica estimable with 2 c.c. of the molybdate solution is 0·060 grm. per litre.

The above procedure does not serve for the estimation of colloidal silica. When this is present, 50 c.c. of the water is heated with 0·2 grm. of powdered sodium hydrogen carbonate in a platinum dish on a boiling water-bath for an hour, addition of 2·4 c.c. of *N*-sulphuric acid then sufficing to neutralise the carbonate added and to redissolve all the silica. When cold, the liquid is made up to 50 c.c. and the total silica then estimated as above. By means of this method it has been found that the silica in ordinary waters exists in the non-colloidal state, that water loses part of its silica when filtered through sand, and that a hot aqueous solution of sodium hydrogen carbonate attacks and dissolves silica from glass vessels. T. H. P.

Agricultural Analysis.

Estimation of Carbon in Soil. L. J. Simon. (*Comptes rend.*, 1923, **176**, 1409–1411.)—The method previously described for estimating carbon (ANALYST, 1922, **47**, 405; 1923, 37), may be applied to soil. From 0·4 to 4 grms. of the soil, according to its content of carbon and to its homogeneity, is introduced into a small conical flask, which contains 25 to 30 grms. of concentrated sulphuric acid and 8 to 12 grms. of silver dichromate, and is connected with a 250 c.c. measuring cylinder. The flask is heated gradually on a water-bath so as to attain the temperature of boiling water in half an hour, this temperature being maintained for four minutes. The volume of the gas in the cylinder is read when cold, and the carbon content calculated. The estimation occupies an hour, and gives results agreeing with those obtained by the cupric oxide method, especially when the soil used has been dried only in the air and not in an oven at 110° C. T. H. P.

Organic Analysis.

Estimation of Acetone and of Ethyl Alcohol in Mixtures of the Two. J. H. Bushill. (*J. Soc. Chem. Ind.*, 1923, **42**, 216–218T.)—Estimation of acetone and alcohol, when present in the same solution, by iodine titration and oxidation

of the alcohol (Northrop, Ashe and Senior, *J. Biol. Chem.*, 1919, **39**, 1) is not satisfactory. The authors' method is to estimate the acetone by Rakshit's method (ANALYST, 1916, **41**, 245) and the alcohol by calculation from the specific gravity by reference to tables showing the density of alcohol-water and acetone-water mixtures. A measured volume of the liquid is taken and about three-fourths of its volume are distilled over and made up to the original bulk and the specific gravity determined. The acetone is now estimated in the distillate by Rakshit's method; reference to the table shows the sp. gr. of a solution of acetone of this strength. The sp. gr. of the alcohol in the mixture is given by 1·00000, plus the sp. gr. of the mixture, minus the sp. gr. of the acetone solution, and from this the percentage of alcohol is found. The sp. gr. of acetone solutions at 15·5° C. are:

Sp. gr.	Acetone per cent. by weight	Sp. gr.	Acetone per cent. by weight
1·00000	—	0·99925	0·538
0·99995	0·040	20	0·576
90	0·080	15	0·609
85	0·120	10	0·643
80	0·160	05	0·677
75	0·198	00	0·710
70	0·235	0·99895	0·744
65	0·270	90	0·777
60	0·303	85	0·811
55	0·337	80	0·845
50	0·371	75	0·878
45	0·404	70	0·912
40	0·438	65	0·940
35	0·471	62	0·962
30	0·505		

H. E. C.

Microchemical Estimation of Hydrocyanic Acid. L. Rosenthaler and K. Seiler. (*Zeitsch. anal. Chem.*, 1923, **62**, 388–389.)—The solution is neutralised in a round flask with a saturated solution of calcium carbonate; 2 to 3 c.c. of pure petroleum spirit are added, and the liquid titrated with 0·001 N iodine solution until the petroleum spirit just shows the faintest coloration: $HCN = I_2 \rightleftarrows ICN + HI$. A blank test should be made with an equal volume of calcium carbonate solution. The iodine solution is standardised against one of hydrocyanic acid obtained by dilution of a stronger solution which has been titrated with 0·02 N silver solution according to Denigès' method. W. R. S.

Estimation of the Soft Resins in Hops. T. K. Walker. (*J. Inst. Brew.*, 1923, **29**, 390–392.)—Twenty grams of the hops are passed through a 20-mesh sieve, and the unbroken seeds and stalks remaining on the sieve are rejected. The finely divided material is weighed, and exactly half the quantity is transferred to a wide-mouthed flask and covered with 199 c.c. of methyl alcohol. After remaining for 24 hours, with occasional shaking, the mixture is filtered, and 100 c.c. of the filtrate are thoroughly shaken with 80 c.c. of petroleum spirit (b. pt. 35–40°C.)

or normal hexane, after which 200 c.c. of ice-cold water are gradually added with frequent agitation.   The aqueous-alcohol layer is run off and extracted with two portions each of 60 c.c. of light petroleum, any emulsion formed being broken down by the addition of a small amount of sodium chloride solution.   The petroleum extracts are mixed, washed with a little water, filtered and evaporated to dryness, and the residue dried to constant weight in an air-oven at 70° C.   This method shows the following advantages over others previously described:—Complete extraction of the resins without the necessity of heating; the necessary operations are reduced to a minimum and the methyl alcohol used has no tendency to induce resinification of the acids.   The results obtained were, in nearly all cases, slightly higher than those given by previous methods.   The total resins present may be estimated by Chapman's method (*J. Inst. Brew.*, 1923, **29**, 388), in which the remaining half of the sifted hops is extracted with warm ether for 5 hours, and an aliquot part of the clear solution is evaporated to dryness.   Higher results are obtained than by the use of whole hops, as used in the original method.   T. J. W.

Spinacene, its Oxidation and Decomposition.   A. Chaston Chapman. (*J. Chem. Soc.*, 1923, **123**, 769–779.)—Further work carried out on larger quantities of spinacene establishes the sp. gr. at 20°/20°C. as 0·858; n_D^{20} as 1·4951; specific rotation, calculated by the $(n^2-1)/(n^2+2)d$ expression, 0·3396; and the molecular refraction as 134·5 ($C_{29}H_{48}$ requiring with six ethenoid linkings R 133·7).   Two determinations of the heat of combustion in a Mahler bomb gave 4388 and 4372 molecular gram-calories respectively.

The dodecabromide is now found to come into line with all the other compounds and supports the formula $C_{29}H_{48}$.   Hydrogenation, oxidation, action of nitric acid, benzoyl peroxide, hydrogen peroxide, decomposition by heat, and bromine derivatives are all discussed and the constitution of spinacene is provisionally put forward as

$$CH_3.CH_2.CH:C(CH_3).CH_2.CH_2.CH.CH_3$$
$$\diagdown CH = CH.C (CH_3) = CH$$
$$| CH_2$$
$$| $$
$$\diagup CH = CH.C (CH_3) = CH$$
$$CH_3.CH_2.CH: C(CH_3).CH_2.CH_2.CH.CH_3$$

D. G. H.

Chemical Constitution of Squalene.   R. Majima and B. Kubota. (*Japan J. Chem.*, 1922, **1**, 19–33.)—A history of previous work is given and reference is made to the constitution of the closely allied or identical substance, spinacene, the subject of various communications by A. Chaston Chapman.   The authors give details of their experimental work in connection with squalene ozonide, its decomposition products, and the dry distillation of squalene.   Squalene hexa-ozonide decomposed in boiling water, with formation of carbon dioxide and formaldehyde, formic acid, acetone, acetone superoxide, succinic acid, lævulinic aldehyde, lævulinic acid, and two acids of unknown constitution, with empirical

formulæ, $C_8H_{14}O_6$ (m.pt. 132–4° C.) and $C_6H_{10}O_5$ (m.pt. 191–2° C.). Lævulinic and succinic acids were present in predominating quantities. The authors regard squalene as a higher aliphatic terpene, probably a dihydro-triterpene, and tentatively suggest a constitutional formula. It was found that when squalene was treated with glacial acetic acid containing sulphuric acid it was converted into a new hydrocarbon containing at least two ring structures in the molecule.

D. G. H.

Inorganic Analysis.

New Sulphonphthalein Indicators for the Determination of Hydrogen-Ion Concentration. *(Chem. Trade J.,* 1923, **72**, 703.)—With a view to improving Clark and Lubs indicator series the following new sulphonphthalein indicators are suggested by B. Cohen *(Public Health Reports*, Feb. 1923, 199).

Chemical Name	Suggested Common Name	Colour Change	Pн. Range
m-Cresol sulphonphthalein.	Meta-cresol purple.	Red to yellow.	0·5–2·5
Dibromo-dichloro-phenolsulphonphthalein.	Brom-chlor phenol blue.	Yellow to blue.	3·2–4·8
Tetra bromo-*m*-cresol sulphonphthalein.	Brom-cresol green.	Yellow to blue green.	4·0–5·6
Dichlorophenol-sulphonphthalein.	Chlor-phenol red.	Yellow to red.	5·0–6·6
Dibromphenol-sulphonphthalein.	Brom-phenol red.	Yellow to red.	5·4–7·0

Brom-cresol green covers the methyl red range, the apparent dissociation constants in terms of P_H being respectively 5·00 and 4·95, and, where the dichromatism of brom-cresol purple is a disturbing factor, brom-phenol red and chlor-phenol red may be used with advantage.

D. G. H.

Indicator for Silver and Halogen Ion Titration. K. Fajaus. *(Chem. Zeit.,* 1923, **47**, 427.)—If a solution of alkaline chloride, bromide, or iodide, containing the sodium salt of fluorescein (in a concentration of about 1 in 40,000) is titrated with silver nitrate, the green colour of the fluorescent solution changes to a red tint immediately the end-point is passed. Addition of a very slight excess of halogen ion restores the original colour. The colour change is due to the fact that the colloidal precipitate adsorbs silver or halogen ion; the adsorbed silver ion is able to combine with the anion of the dye to form a salt which possesses a red colour. Excess of halogen ion again decomposes the coloured silver salt. Eosin (tetrabromofluorescein) cannot be used for chlorine, and erythrosin (tetraiodofluorescein) only for iodine ion titrations, which is explained by a decrease in the faculty of adsorption in the order Cl–Br–I.

W. R. S.

Volumetric Estimation of Gold. W. B. Pollard. *(Bull. Inst. Min. Met.,* April, 1923.)—The *aqua regia* solution, containing less than 0·005 grm. of gold, is evaporated in a small flask till only a few drops remain. Addition of 2 c.c. of a 1 per cent. paraldehyde solution destroys any nitrous acid present, after which the flask is allowed to stand for a few minutes. Twenty-five c.c. of water are added, followed by a few drops of very dilute silver nitrate solution (which acts as a catalyst) and 1 c.c. of a 0·1 per cent. solution of *o*-toluidine in 10 per cent.

hydrochloric acid as an indicator; a strong yellow colour is produced, which is just discharged by titration with a standard solution of methyl-p-aminophenol hydrochloride (metol). This solution contains 1·284 grms. of metol in 1000 c.c. of 2 per cent. hydrochloric acid by volume; 1 c.c. =0·0010 grm. of gold. When the yellow colour has just disappeared, the solution is heated to 40° C.; any slight yellow tint thus produced is finally discharged by cautious further titration. Copper in quantity exceeding that of the gold gives high results; iron gives with o-toluidine a slight yellow colour which can be removed by addition of ammonium fluoride. W. R. S.

New Method of Estimating Arsenic in Steels. C. Mazzetti and P. Agostini. (*Gazz. Chim. Ital.*, 1923, **53**, I., 257–261.)—The following procedure gives results agreeing well with those obtained by the Ledebur method commonly used in steel-works, and has the advantages of being more easily carried out and of avoiding danger of loss of arsenic when the heated residue is taken up in hydrochloric acid:—Ten grms. of the steel turnings are treated in a covered porcelain basin with 80 c.c. of *aqua regia* ($1HNO_3 + 3HCl$), which is added a little at a time. The solution obtained is evaporated to dryness on a sand-bath, the residue taken up in 60 to 80 c.c. of hydrochloric acid, and the solution filtered through a Gooch crucible to remove silica and carbon. The filtrate is mixed with 75 c.c. of Bettendorf's reagent (400 grms. of stannous chloride dissolved in 1000 c.c. of hydrochloric acid of sp. gr. 1·18) in a 500 c.c. flask, which is closed with a glass pear and heated in a water-bath at 40–50° C. until all the arsenic settles to the bottom. The liquid is filtered, with slight suction, through a Berzelius paper, and the arsenic washed free from iron, the filter and precipitate being shaken with 20 to 30 c.c. of water in a 100 c.c. flask until the paper is pulped. The arsenic is then dissolved in 10 to 15 c.c. of 0·1 N iodine solution and the excess of iodine estimated by titration with standard arsenite solution in presence of phosphate or sodium hydrogen carbonate and starch paste until a yellowish pink coloration is obtained (*cf.* Andrews and Farr, *Zeitsch. anorg. Chem.*, 1909, **62**, 123). T. H. P.

Reducing Action of Ferrous Hydroxide. New Method of Estimating Nitrites and Nitrates. S. Miyamoto. (*Japan. J. Chem.*, 1922, **4-5**, 57–80.)— *Nitrites.*—Two hundred c.c. of a saturated solution of sodium hydroxide, to which about 0·1 to 0·3 grm. of nitrite and 15 grms. of ferrous sulphate have been added, are boiled for 30 to 45 minutes, the ammonia evolved absorbed in sulphuric acid of known strength, and the excess of acid titrated back with sodium hydroxide solution. Four experiments with sodium nitrite gave an average of 20·24 per cent. of nitrogen, as against a calculated value of 20·30 per cent. *Nitrates.*—Owing to the slower reduction, the process requires some modification. As before, the mixture of nitrate (0·1 to 0·3 grm.), ferrous sulphate (15 grms.) and 200 c.c. of a saturated solution of sodium hydroxide is boiled, but for 3 to $3\frac{1}{4}$ hours, and at the same time hydrogen, and nitrogen or air are passed through the boiling liquid. An extra reflux condenser is fixed to the boiling flask between it and the ordinary

condenser and, after boiling for 3 to $3\frac{1}{4}$ hours, the water is turned off the reflux condenser so as to drive all ammonia into the sulphuric acid vessel. Four experiments showed an average molecular concentration for potassium nitrate of 0·0993, as against 0·1000 calculated.   D. G. H.

Volumetric Estimation of Hypochlorous Acid. A. Schleicher. (*Zeitsch. anal. Chem.*, 1923, **62**, 329–335.)—Clarens' modification (*J. Soc. Chem. Ind.*, 1915, **34**, 547) of Penot's arsenite method was tested, as well as Penot's original method, by means of Treadwell's electrometric process (ANALYST, 1921, **46**, 301). The use of a mechanical stirrer in the solution diluted to 250 c.c., and the circumstance that no external indicator is required, enable the estimation to be carried out in a very short time, and the differences between the results obtained by the two methods become insignificant. The evolution of chlorine peroxide during the titration, described by Clarens, could not be observed; the addition of potassium bromide as indicator, recommended by the same author, was found to present no advantage and to lead to slightly low results.   W. R. S.

Volumetric Estimation of Phosphorous Acid in Presence of Phosphoric Acid. A. Wingler. (*Zeitsch. anal. Chem.*, 1923, **62**, 335–337.)—The method consists in oxidising phosphorous acid by means of bromine, and titrating the hydrobromic and phosphoric acids formed. A measured volume of the solution is digested for 10 minutes with freshly-prepared bromine water (10 to 15 c.c. per 0·1 grm. H_3PO_3) in a suction flask at ordinary temperature. The flask is wrapped in paper so as to prevent any action of the light. The excess of bromine is removed by a vigorous air current passing through a capillary dipping into the liquid. When colourless, the liquid is titrated with 0·1 N sodium hydroxide solution, first with addition of methyl orange, then with phenolphthalein. Twice the number of c.c. consumed between the two end-points corresponds to the phosphoric acid formed *plus* that originally present, while the difference between the total number of c.c. and the above product corresponds to hydrobromic acid, and hence to the phosphorous acid: $H_3PO_3 + H_2O + Br_3 = H_3PO_4 + 2HBr$. 1 c.c. 0·1 N NaOH = 0·004103 grm. H_3PO_3, or 0·004903 grm. H_3PO_4. The phosphoric acid originally present is found by difference.   W. R. S.

Analysis of Titanium Pigments. L. E. Barton. (*Chem. Trade J.*, 1923, 357–358.)—The following volumetric method of estimating titanium in titanium pigments is not affected by other elements likely to be present, and is convenient when a number of samples have to be analysed. The reagent used is prepared by dissolving 30 grms. of ferric ammonium sulphate in 300 c.c. of water containing 10 c.c. of sulphuric acid, adding permanganate solution drop by drop as long as the pink colour disappears, diluting to a litre, and standardising in terms of iron. 0·5 grm. of the pigment is mixed with 20 c.c. of concentrated sulphuric acid and 7 to 8 grms. of sodium sulphate in a 250 c.c. beaker, which is heated on a hot plate until fumes of sulphur trioxide are evolved and then boiled over a flame for 5

minutes or until solution is complete. The cold liquid is mixed with 100 c.c. of water and boiled, the barium sulphate and silica being filtered off and washed with .5 per cent. sulphuric acid solution. As reductor a 500 c.c. pyrex glass dispensing burette, 22 by 1 inches is used. Into this is introduced a platinum gauze covered with a $\frac{1}{4}$-inch mat of fibrous asbestos supporting, in the order mentioned, a 1-inch layer of 10-mesh and a 6-inch layer of 20-mesh amalgamated zinc and a 5-inch layer of amalgamated stick zinc. The reductor is connected with a litre flask for receiving the reduced titanium solution through a 3-holed rubber stopper, which carries also an inlet tube for carbon dioxide and an outlet tube joined to the suction pump. The reductor is prepared by passing through it a little hot dilute sulphuric acid followed by hot water, sufficient of which is left to cover the zinc. The hot filtrate from the barium sulphate is now introduced, about 100 c.c. of water being drawn from the reductor into the original beaker to bring the solution to about the top of the zinc; the water withdrawn may be acidified with 10 c.c. of sulphuric acid and kept on a hot plate for washing after the reduction. The titanium solution is left in the reductor for 10 minutes, the receiving flask being meanwhile connected with the reductor and the air displaced by carbon dioxide. When reduction is complete the receiving flask is joined to the suction pump, and, with carbon dioxide still flowing, the reduced solution is drawn out and is followed by the acid washing liquor and three or four quantities of 100 c.c. of hot water, the zinc being kept covered. The suction is then gradually released and the flask disconnected, 5 c.c. of saturated potassium thiocyanate solution being added and the liquid titrated at once with the ferric ammonium sulphate solution until a brownish colour persists for at least a minute; the burette reading is to be corrected by an amount which each operator must determine by means of several blank tests. As the composition of titanium oxide is always very nearly 25 per cent. of titanic oxide and 75 per cent. of barium sulphate, the percentage of the pigment is obtained nearly enough for all practical purposes by multiplying the percentage of titanic oxide by four.

If only an occasional estimation is to be made, the following gravimetric method is useful. The filtrate from the barium sulphate (see above) is treated with excess of ammonia and filtered, the precipitate being dissolved in hydrochloric acid (1:1) and again precipitated with ammonia. The precipitated titanium hydroxide is filtered off and washed with hot water, the filtrate being added to that from the previous filtration. The residue is dissolved in hydrochloric acid (1:1), the volume of the solution, which is received in a 500 c.c. beaker, being kept below 150 c.c. To the solution, heated to 50° C., ammonium hydroxide is added gradually until the precipitate formed just redissolves, ammonium carbonate solution being then added, drop by drop, until a slight permanent precipitate forms. This is dissolved in hydrochloric acid, and an excess of 2 c.c. of the acid (1:1) added, the solution being treated with sulphur dioxide gas or solution until it smells strongly, diluted to about 400 c.c., and boiled until only a slight odour remains. The liquid is filtered while hot, and the precipitate washed with hot water, dried, calcined at not lower than 900° C. for 30 minutes and weighed as TiO_2.

With a mixed pigment containing titanic oxide, 1 grm. is heated on a hot plate in a 400 c.c. pyrex glass beaker with 10 grms. of sodium sulphate and 40 c.c. of sulphuric acid (93 per cent.) for 30 minutes, and then boiled for about 10 minutes, cooled, diluted to 300 c.c., boiled for 20 minutes, and filtered while hot. The residue is washed with 5 per cent. sulphuric acid solution; it contains silica, undecomposed silicates and all the lead and barium as sulphates. The hot filtrate, containing the titanium, iron, aluminium, zinc, and calcium, is treated with excess of ammonia, and filtered, the precipitate being washed with hot water, redissolved in hydrochloric acid (1:1), and again precipitated with ammonia. The precipitate is filtered off and washed with hot water, the filtrate being united with that from the first separation; if desired, this filtrate may be tested for aluminium and used for estimating the calcium and zinc. The precipitate is dissolved in dilute hydrochloric acid, and the titanium separated and estimated as described above, the filtrate being used for estimating the iron and aluminium.   T. H. P.

Physical Methods, Apparatus, etc.

Measurement of the Colour of Brown Solutions with special Reference to Tannin Extracts. H. R. Procter. (*J. Soc. Chem. Ind.*, 1923, **42**, 73–79.)—The basis of analytical and synthetical methods of colour measurement is discussed, and a new method is described which is entirely independent of artificial and arbitrary standards in that the measurement is of the depth of the extract solution required to absorb one half or other suitable fraction of the light at three or four selected portions of the spectrum, say red, yellow, green and blue. The reciprocal of the depth $\times$ concentration represents the absorptive power per unit Ct for the particular spectrum colour observed. The colour screens may be calibrated by reference to standard flames. The standard colour is that of a 20 per cent. iron ammonium alum solution, and any good colorimeter provided with three colour screens may be used. The colour value is obtained by dividing the depth of iron solution in mm. by the thickness, also in mm. of the extract solution required to match it, using each colour, red, blue, and green. The iron alum solution must not be diluted. Numbers greater than unity represent tanning solutions darker than the standard and *vice-versa*; redness or greenness is judged by the relative proportions of the red and green. For the estimation, it is convenient to put the iron solution in the variable cell and match it with extract solutions of suitable concentrations in cells of known thickness. An example makes the method clearer:—A gambier solution containing 0·42 per cent. of tannin was used in a 14 mm. cell, the depths of iron solution required to match it, with the use of the screens were:—Red 6·1 mm., green 6·8 mm., and blue 10·1 mm. The colour was therefore $6·1 \div 14 = 0·44$ red, $6·8 \div 14 = 0·49$ green, and $10·1 \div 14 = 0·78$ blue. To obtain the colour of a 0·5 per cent. solution of tannin these figures were multiplied by 50/42. Each colour being less than 1, the solution was lighter in colour than the standard iron alum solution.   H. E. C.

Sublimation as an Analytical Procedure. J. Hortvet. (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 481–489.)—The apparatus used consists of a glass vessel A fitted with a condenser and tube for connection to a vacuum pump, the lower rim being ground to fit the neck of the lower section B. The material under examination, mixed with sand or magnesia, is placed in the glass dish C, this being held between the lower rim of A and the spring tripod below, whilst a porous diaphragm of 100-mesh platinum gauze E prevents any condensed sublimate from falling into the dish. The lower portion of the sublimation cell is heated in a copper cup of adjustable height, which is fitted into a vertical metal cylinder containing a small gas burner. For micro-sublimation a glass capsule, shown by the dotted line, is supported in the spring tripod and covered by a micro slide D, upon which the sublimate is condensed. The temperature of sublimation is indicated by a thermometer placed in the heating cup. Applications of the apparatus in the qualitative and quantitative estimation of volatile substances are given, the maximum error with materials containing known amounts of santonin, camphor and benzoic acid not exceeding 1·3 per cent. By rapid sublimation *in vacuo* substances possessing high vapour pressure, such as caffeine, theobromine, cantharidin, etc., may be obtained as definite crystalline deposits.　　　T. J. W.
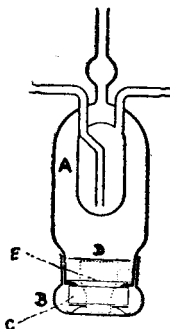
Laboratory Device for Delivering Heavy and Corrosive Liquids. A. P. Harrison. (*J. Ind. Eng. Chem.*, 1923, **15**, 497.)—A graduated cylinder is closed at the bottom with a one-hole rubber stopper and a glass plate is placed inside the cylinder over the hole, forming the valve *V* (see illustration). The top of the cylinder is fitted with a rubber stopper carrying the delivery tube *D* and the T-tube *P*, one arm of the latter being connected with a compressed air supply. When the lower end of the cylinder is immersed in a liquid this rises in the cylinder through the valve until it is stopped by cutting off the air outlet at the base of the tube *P*; if the finger is now placed over the open end of the T-tube, the compressed air causes the valve to close and forces the liquid out of the delivery tube. The tube *P* may be adjusted at such a height that any desired volume of liquid may be measured and delivered.　W. P. S.
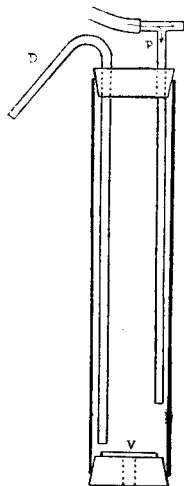
Use of the Bunsen Valve in Connection with a Filter Pump. F. W. Ashton. (*J. Ind. Eng. Chem.*, 1923, **15**, 481.)—A Bunsen valve fitted in a bottle connected by tubing with the water-pump and the vessels to be exhausted prevents variations in the pressure due to differences in the pressure of the water-supply. A safety bottle is fitted between the valve bottle and the pump, and a third bottle may be placed in the series to serve as a "vacuum" reservoir.　　　W. P. S.

Apparatus for Delivering Concentrated Sulphuric Acid and Sodium Hydroxide Solutions. R. C. Abbott. (*J. Ind. Eng. Chem.*, 1923, **15**, 493.)—A large bottle serving as the reservoir for the solution is closed with a rubber stopper through which pass three tubes. One of these reaches from the bottom of the bottle, its outer end being bent so that it enters the top of a burette and reaches exactly to the zero mark. A second tube is connected with a hand pump supplying compressed air; the third tube is left open. On closing the open end of this tube with the finger and forcing air into the reservoir, the liquid in the latter passes over into the burette; when this is filled, the finger is removed, the pressure is released immediately, and any excess of solution in the burette siphons back into the reservoir, leaving the burette filled exactly to the zero mark.

W. P. S.

Procedure for Opening Explosive Engines from a Distance. G. A. Le Roy. (*Ann. Falsificat.*, 1923, **16**, 147–148.)—The suspected engine (A) of iron, steel or other metal which may contain explosives is, after X ray examination, varnished, and the upper part protected by a wrapping (R) of rubber or bakelite. A wire lead is connected with A and a circular patch S is scraped clean to facilitate attack by acids; then it is immersed up to S in a suitable vessel containing carbon tetrachloride, above which is a layer of dilute acid—or alkali according to the nature of the metal. A lead electrode B is connected with the negative terminal of two accumulators or other source of a weak current, and serves as the cathode (see figure). The whole is put in a safe place surrounded by sand bags, and the current switched on; after some hours or days the metal will be dissolved away at S, and the lower part will automatically be removed from the action of the acid by the carbon tetrachloride. A mirror and telescope can be arranged, if it is desired to observe the process.
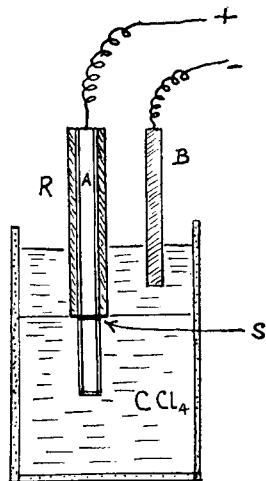
H. E. C.

Reviews.

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. Vol. III. By J. W. MELLOR, D.Sc. Pp. x.+927. London: Longmans, Green & Co. 1923. Price £3 3s. net.

Volume III. of this great work has now appeared, and we are informed that Volume IV. is in the press. This is further evidence of the untiring energy with which the author is devoting himself to the colossal task he has undertaken. Moreover, the high standard and comprehensive treatment exemplified in the previous volumes are maintained in the one under review, and the style, so

peculiar to the author, makes the reading of the volumes very fascinating. The relatively few quotations met with in this volume, as compared with the profusion found in the first two, is, however, very noticeable. There can be little doubt that when Dr. Mellor's treatise is finished it will be the most complete survey of inorganic chemistry which has yet appeared. The copious lists of references given in Volume III., as in Vols. I. and II., are exhaustive, and thereby make it an efficient key to the whole literature of the subjects dealt with.

The present volume deals with copper, silver and gold, treated separately, and the alkaline earths treated comparatively, together, with some little treatment of theoretical subjects relating to the different topics as they arise. Of these, the most important is an outline of the chemistry of colloids, about 30 pages in length, given in the chapter on gold.

Omissions and errors are very hard to find. The reviewer feels, however, that insufficient attention has been given to the recording of solubility product data. The solubility data appear to be given fully, but this does not seem to be the case in regard to the solubility products. This is perhaps due to Dr. Mellor's personal views on the subject (*vide* Vol. I., pp. 997–999). From that discussion, the impression left on the reader's mind is that the solubility product principle is empirical and, at best, that any values assigned to the solubility product for any particular compound would only be approximate. For cuprous and cupric hydroxides no data of either their solubility or solubility products are given, although the latter were determined and published in 1909.

The volume is full of information of value to the analyst. In each of the chapters dealing with the different elements an important discussion is included on "Reactions of Analytical Interest," and, needless to say, there is considerable detail to be found scattered throughout the volume which has some bearing on analytical chemistry.

The index seems to be the weak part of the volume. Although the index extends over 19 pages, many a subject which is discussed quite adequately in the text is often not mentioned, *e.g.* the analytical reactions already alluded to. It should be said, however, that the system employed throughout the text of printing suitable words in heavy type to indicate the matter dealt with, tends to compensate for the scanty index in facilitating rapid reference.

In conclusion, Dr. Mellor must be heartily congratulated for the exceptional service he is doing to students of chemistry.

HUBERT T. S. BRITTON.

A TEXT BOOK OF INORGANIC CHEMISTRY. New and enlarged edition. By G. S. NEWTH, F.I.C. Pp. 772. London: Longmans, Green & Co. Price 8s.

First published in 1894, and running through eleven editions in as many years, this book requires no general description. The present new and enlarged edition contains some fifty extra pages, due to the insertion of three additional chapters. The first of these deals with the Phase Rule, and should give the reader a good

opportunity of obtaining a grasp of the underlying principles; the second in-troduces modern views of the structure of the atom and the electronic theory of valency; the third chapter gives an account of the radioactive elements in detail sufficient for the majority of students.

As one would expect in a book of this standing, very few errors were noticed, such as, for example, in the case of the constant for the volume of gramme molecular weights of gases, which is given as 22·25. Obviously the intention of the writer is to bring his book up to date, and in many respects he has undoubtedly succeeded. In several cases, however, further revision is highly desirable. Three examples may be given; no reference is made to the recent work of Onnes on very low temperatures; the modern method for the manufacture of oxygen is not given, though no less than fourteen methods of formation are mentioned; recent processes for the manufacture of nitric acid receive only one short paragraph. When the size of a volume must be kept within certain limits, as is necessary in a book of this type, it must always be difficult to decide what to include and what to leave out; in successive editions the description of out-of-date methods should be cut down or omitted in order to find room for more recent work. The examples quoted above lead one to doubt whether the author has been altogether successful in his revision; nevertheless the book may be recommended as suitable for students towards the end of their school career and at the beginning of their university training. The general style of the book and most of the illustrations are the same as in former editions. A. F. KITCHING.

SURFACE TENSION AND SURFACE ENERGY, AND THEIR INFLUENCE ON CHEMICAL PHENOMENA. R. S. WILLOWS, M.A., D.Sc., and E. HATSCHEK. Third Edition. Pp. viii.+136, with 25 Illustrations. London: J. &. A. Churchill. 1923. Price 6s. 6d. net.

The third edition of this well-known book has been revised and considerably enlarged by Dr. Willows. The authors state that "the object of the work is to give the student of chemistry an adequate idea of the fundamental laws of surface tension and surface energy, while avoiding the purely mathematical exercises which occupy so much of the space devoted to the subject in text books of physics, and then to deal at some length with the relations between surface energy and such constants and phenomena as are likely to be of interest to the chemist and biologist."

The authors have succeeded admirably in presenting a lucid, accurate and most interesting account of surface tension principles and phenomena. The new edition includes even very recent work, and offers a clear introduction to the newer ideas on thin films, molecular orientation, and boundary lubrication. The work of Langmuir, Harkins, Adam and Hardy in this connection is briefly but concisely summarised.

At this time, when the physical chemistry of interfaces is assuming such importance, students of colloid chemistry and physiology will do well to peruse so helpful an introduction to an important subject. WILLIAM CLAYTON.

BELL'S SALE OF FOOD AND DRUGS ACTS. By C. F. LLOYD, with Chemical Notes by R. A. ROBINSON. 7th Edition. Pp. xxv. and 373 and 54. London: Butterworth & Co., Bell Yard, Temple Bar, W.C.2. 1923. Price 15s. net.

A new edition of "Bell" will be welcomed by all those who are in any way responsible for the working of the Food and Drugs Acts in this country. A vast amount of legislation has appeared in this field since the last edition, an amount which is only partially indicated by the increase in the number of pages (from 310 in the last edition to 373 in the present one, in spite of there being slightly more lines to the page and the "Introduction" having been left out), since much of the emergency legislation has since been repealed. The somewhat complicated nature of the various orders and the method of their repeal has made the use of some such authoritative work as the present absolutely essential to any one who wishes to know exactly what orders are in force at the present time, and what interpretation has been put upon them by the Courts.

The present volume has been brought quite up to date and contains, among others, the Milk and Dairies (Amendment) Act, 1922, together with the orders made under that Act. The notorious circular of July, 1922, concerning Milk Prosecutions, is also included, but, unfortunately, the somewhat belated, but very necessary, withdrawal of this circular took place after the date of publication of this volume, so that it could not be included. The case law has been brought up to date, and forty-one new cases are included and suitably commented upon. The completeness of these cases and the manner in which cross references are given is a valuable feature of the work. The chemical notes of Mr. Robinson occupy some twenty-four pages, and contain a quantity of condensed information which, elsewhere, is frequently most elusive when most required. They will doubtless be a source of inspiration to zealous inspectors who desire to extend the scope of their sampling.

The form of certificate given on page 109 for a milk deficient both in fat and solids-not-fat seems somewhat unnecessarily involved; it would seem to be equally unobjectionable and considerably clearer to the bench if, after setting out the constituents of the milk into fat, solids-not-fat and water, the analyst continued "Comparison of the above results with the minimum limits fixed by the Sale of Milk Regulations, 1901, viz.: Solids-not-fat 8·5 per cent., fat 3·0 per cent., shows that the said sample of milk was deficient of 15·6 per cent. of the minimum amount of fat and 8·8 per cent. of the minimum amount of solids-not-fat. The deficiency of solids-not-fat is equivalent to 8·8 per cent. of extraneous water." The form for diluted whisky on the same page should be modified for the standards given in the Licensing Act, 1921, namely, 35° u.p., which are correctly given on page 188.

The book is clearly printed, well bound and reasonably free from misprints, although the attention of the compositor apparently wandered when he was dealing with the last few lines on page 337; it is a worthy successor to previous editions.

G. D. ELSDON.

REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY. Issued by the Society of Chemical Industry. Vol. VII., for 1922. Pp. 569. Price 7s. 6d. to Members; 12s. 6d. to Non-Members.

The arrangement of the twenty-four sections into which this volume is divided follows closely the sequence of the Abstracts in *Chemistry and Industry*. The separate section on Analytical Chemistry is now omitted, this part of the work being covered in the Reports of the Chemical Society for 1922, in which this section has again been written by Mr. C. A. Mitchell.

Many notes on analysis will be found under the various headings; and sub-sections headed "Analytical" are to be found in the articles on Rubber, Soils and Fertilisers, Foods, Leather and Glue.

The article on Glass by Dr. M. W. Travers gives a summary of the work carried out during the year on testing the resistance of glass-ware to attack by chemicals. It is disappointing to read here that little original work on optical glass has been published recently.

In the article on Foods, Dr. G. W. Monier-Williams summarises recent advances in our knowledge of vitamins, canned foods with special reference to botulism, storage of fruit, and milk and dairy produce. Recent American work is here mentioned which apparently shows that, for the prevention of rickets, exposure to sunlight (*cf.* Abstract, p. 392) is essential, and of more importance than the presence of vitamin A in the diet; thus confirming what Noel Paton, Findlay and others have maintained, viz. that the chief causes of rickets are confinement, lack of fresh air and exercise.

References to the prevalent decline of trade are frequent in the various sections.

Every chemist, no matter in what special direction his work may lie, will find much of the greatest interest in the chapters on Plant and Machinery, Fuel, Gas, Iron and Steel, Leather, and Rubber.

The type is clear and the binding attractive. It would be advisable to enlarge the type of the numerals for the volume number and year of issue on the back of the cover, as these figures are, at present, barely visible at some little distance from the bookshelf. R. LEITCH MORRIS.

Publications Received.

WAVE-LENGTH TABLES FOR SPECTRUM ANALYSIS. Compiled by T. TWYMAN. Pp. 106. London: A. Hilger, Ltd. Price 7s. 6d.

THE BRITISH PHARMACEUTICAL CODEX. 1923. Pp. 1669. The Pharmaceutical Society. Price 30s. net.

LES ISOTOPES. By A. DAMIENS. Pp. 118. Paris: Gauthiers-Villars et Cie. 1923. Price 12 fr.

PERFUMES AND COSMETICS (WITH ESPECIAL REFERENCE TO SYNTHETICS). By W. A. POUCHER. Pp. 462. London: Chapman & Hall. 1923. Price 21s. net.

THE DESTRUCTIVE DISTILLATION OF WOOD. By H. M. BUNBURY. Pp. 320. London: Benn Bros. 1923. Price 35s. net.

YEAR BOOK OF PHARMACY FOR 1922. Pp. 546. London: J. & A. Churchill.
INORGANIC COMPLEX COMPOUNDS. By R. SCHWARZ. Translated by L. W. BASS.
Pp. 82. London: Chapman & Hall. Price 8s. 6d. net.
COURS DE CHIMIE ORGANIQUE. By F. SWARTS. 3rd Edition, Vol. I., 1921, pp. 674.
Vol. II., 1922, pp. 734. Brussels: M. Lamertin. Price 50 fr. each vol.
THE CHEMISTRY OF UREA. By E. A. WERNER. (Monographs on Biochemistry.)
Pp. 212. London: Longmans, Green & Co. Price 14s. net.
BLOXAM'S CHEMISTRY, INORGANIC AND ORGANIC. 11th Edition. Edited by
A. G. BLOXAM and S. JUDD LEWIS. Pp. 832. London: J. & A. Churchill.
1923. Price 36s. net.
BUREAU OF MINES. DEPT. OF THE INTERIOR, U.S.A.
BULL. 211. THE CHLORIDE VOLATILISATION PROCESS OF ORE TREATMENT.
G. T. VARLEY, E. P. BARRETT and R. H. BRADFORD.
BULL. 213. TALC AND SOAPSTONE. THEIR MINING, MILLING PRODUCTS,
AND USES. By R. B. LADOO. ,
BULL. 216. BIBLIOGRAPHY OF PETROLEUM AND ALLIED SUBSTANCES IN
1919 AND 1920. By E. H. BURROUGHS.
BULL. 217. PREPARATION, TRANSPORTATION AND COMBUSTION OF POWDERED
COAL. By J. BLIZARD.
BULL. 218. THE TECHNOLOGY OF SLATE. By O. BOWLES.
TECHNICAL PAPER 300. THE UNIVERSAL AND THE FIREMAN'S GAS MASKS.
By S. H. KATZ, J. J. BLOOMFIELD and A. C. FIELDNER.
REPORT ON THE ACTIVATED SLUDGE PROCESS OF SEWAGE PURIFICATION. ITS
EFFICIENCY AND APPLICABILITY TO THE GLASGOW WORKS. By F. W.
HARRIS.
TRANSPARENT PREPARATIONS OF COAL FOR MICROSCOPICAL INVESTIGATIONS. By
J. LOMAX and J. R. LOMAX. (The Lancashire and Cheshire Coal Research
Association.) London: Witherby. Price 2s. net.
THE DETERMINATION OF CARBON MONOXIDE IN VITIATED AIR. INCLUDING THE
ANALYSIS OF MINE GASES. By F. S. SINNATT and L. SLATER. (The
Lancashire and Cheshire Coal Research Association.) London: Witherby.
Price 2s. net.

The Institute of Chemistry of Great Britain and Ireland.

PASS LIST.

JULY EXAMINATIONS: 1923.

The following candidates have passed the examination for the Associateship:—
In General Chemistry: A. C. Anderson, J. Barnett, H. G. Beard, W. F. Bennett,
W. Booth, T. H. Bott, F. J. Bubb, R. Child, W. Crombie, B. W. A. Crutchlow,
R. H. Curtis, P. Faichney, A. W. Fairgrieve, A. T. Groves, A. N. Harrow, S.
Hibbert, H. E. Hill, N. E. Jones, L. G. Kimmins, C. S. Kirby, W. M. Laing, P. J.
Leaper, R. Lindsay, J. McGrath, A. P. Mieras, M. A. Mosley, R. B. Moyes, J. H.
Oliver, D. Paul, A. Pound, J. A. H. T. Rosewarne, W. L. Russell, H. N. Saunders,
R. Scott, C. G. Smith, Miss S. M. L. Snelus, G. D. D. W. Thacker, B. Thomas,
H. Threadgold, J. D. Tully, J. Walker, W. H. Wells, A. S. Wilkie, G. E. Wilson,
T. Wood, and A. R. Wylie. *In Branch (b), Metallurgical Chemistry*: T. G. Howard.
In Branch (e), Chemistry, including Microscopy, of Food and Drugs and Water:
J. E. Woodhead. *In Branch (g), Chemical Technology*: G. F. Martin.
The following Associates have passed the examination for the Fellowship:—
In Branch A, Inorganic Chemistry: N. Hackney and W. O. R. Wynn. *In
Branch C, Organic Chemistry*: A. Cohen. *In Branch D, Agricultural Chemistry*:
J. E. Ritchie.