JUNE, 1929. Vol. LIV., No. 639.

THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 1st, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—John William Haigh Johnson, M.Sc., F.I.C., Mamie Olliver, B.Sc., A.I.C., and George Edward Shaw, B.Sc.

Certificates were read for the second time in favour of:—Alfred Norman Leather, B.Sc., F.I.C., Richard Harold Morgan, B.Sc., A.I.C., and William George Painton, B.Sc., A.I.C.

The following were elected Members of the Society:—Peter Trevisa Clarke, B.A., Alfred Clive James, B.Sc., A.I.C., Herman Lee, B.Sc., A.I.C., James Frederick Morse, Lawrence John Odling, Willie Horner Wilkinson.

The following papers were read and discussed:—"The Determination of Organic Peroxides," by R. S. Morrell, M.A., Ph.D., F.I.C., and S. Marks, M.Sc., A.I.C.; "Differential Halogen Absorption of Oils and Fats," by J. W. Croxford (Work done under the Analytical Investigation Scheme); "A New Method for the Separation of Small Quantities of Tantalum and Niobium from Titanium," by W. R. Schoeller, Ph.D., and C. Jahn (Work done under the Analytical Investigation Scheme); and "The Analysis of Small Samples of Gas," by H. R. Ambler, B.Sc., A.I.C.

The Alkaloid Test for Tannins.

By CHRISTINA MARY FEAR, B.Sc.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, March 6, 1929.)

F. A. A. Meyer (*Crell's Ann, Chem.*, 1791, Part I, 43) seems to have been the first to have recorded the observation that an infusion of cinchona bark is precipitated by an infusion of gall nuts. This was confirmed by Duncan (*Nicholson's J.*, 1803, **6**, 225), Fourcroy and Vauquelin (*Bull. Pharm.*, 1810, **2**, 241), Pelletier and Caventou (*Ann. Chim. Phys.*, 1820, **15**, 2891), and Henry and Plisson (*J. Phar.* 1827, **13**, 268). Later, the use of quinine as a reagent for the detection of tannins was suggested by Pelouze (*Ann. Chim. Phys.*, 1834, **57**, 423), and this base was subsequently referred to as Pelouze's reagent by Henry (*J. Pharm.*, 1835, **21**, 213), who made the sweeping statement that all alkaloids are precipitated by tannins, a view now widely accepted by workers on tannin chemistry. In the course of some work carried out by Mr. A. E. Jones in this laboratory it was, however, noticed that pilocarpine was not precipitated by gallotannin, and at the suggestion of Dr. Nierenstein an investigation was undertaken to see how far the generally accepted view is correct.

The following table gives the results obtained by using a 1 per cent. gallotannin solution, made up as follows:—The weighed gallotannin was washed into a graduated flask with hot distilled water until all had dissolved, the solution was cooled, and made up with cold water. All alkaloids investigated were obtained from the British Drug Houses in the form of their hydrochlorides; experiments were carried out at room temperature.

The following results were obtained on adding 2 c.c. of 1 per cent. gallotannin solution to the different alkaloids:—(*See table on next page.*)

This tannin was a commercial specimen of Schuchardt's gallotannin from Chinese galls. As a check, further experiments were made with pilocarpine and papaverine hydrochlorides, the following gallotannins being used:

(1) Schuchardt's gallotannin, purified according to Emil Fischer's method.

(2) Mitchell's gallotannin (*i.e.* gallotannin practically free from glucose).

(3) A specimen of gallotannin prepared from Basra galls (Aleppo gallotannin) in this laboratory (*i.e.* gallotannin which contains ellagic acid in addition to gallic acid in its molecule).

The results were identical in all cases.

Alkaloid.	Concentration of Alkaloid Solution.					
	10 per cent.	Saturated below 10 per cent.	1 per cent.	Saturated below 1 per cent.	0·1 per cent.	0·01 per cent.
Aconitine.	No ppt.		No ppt.		No ppt.	No ppt.
Apomorphine	,,		,,		,,	,,
Atropine.	Very slight opalescence.		Very slight opalescence.		,,	,,
Berberine.				No ppt.		
Betaine.	No ppt.		No ppt.		No ppt.	No ppt.
Brucine.	Heavy white curdy ppt.		Heavy white curdy ppt.		Heavy white curdy ppt.	Heavy white curdy ppt.
Caffeine.	Heavy white curdy ppt.		Heavy white curdy ppt.		Heavy white curdy ppt.	No ppt.
Cinchonidine.		Heavy yellowish white colloidal ppt.	White colloidal ppt.		White colloidal ppt.	Very slight opalescence.
Cinchonine.		Heavy yellowish white colloidal ppt.	Heavy yellowish white colloidal ppt.		Yellowish white colloidal ppt.	No ppt.
Cotarnine.	Very slight opalescence.		Very slight opalescence.		No ppt.	No ppt.
Emetine.	Slight opalescence.		Slight opalescence.		Slight opalescence.	Slight opalescence.
Ephedrine.	Very slight opalescence.		Very slight opalescence.		No ppt.	No ppt.
Homatropine.	No ppt.		No ppt.		No ppt.	No ppt.
Hydrastine.	Slight opalescence.		Slight opalescence.		Very slight opalescence.	Very slight opalescence.
Hydrastinine.	No ppt.		No ppt.		No ppt.	No ppt.
Narceine.				Slight opalescence.		
Narcotine.	No ppt.		No ppt.		No ppt.	No ppt.
Papaverine.	,,		,,		,,	,,
Pilocarpine.	,,		,,		,,	,,
Quinine.	Heavy yellowish white flocculent ppt.		White colloidal ppt.		White colloidal ppt.	Slight opalescence.
Strychnine.	Heavy white curdy ppt.		Heavy white curdy ppt.		Heavy white curdy ppt.	Heavy white curdy ppt.
Tropacocaine.	No ppt.		No ppt.		No ppt.	No ppt.
Yohimbine.	,,		,,		,,	,,
Cocaine.	Very slight opalescence.		Very slight opalescence. Sat. at 1 per cent.		,,	,,
Dimorphine.			No ppt.		,,	,,
Morphine.			,,		,,	,,

From these experiments it is evident that the only alkaloids giving appreciable precipitates with tannin solutions are brucine, caffeine, cinchonine and cinchonidine, quinine and strychnine. The possible relationship between the structure of alkaloids and their precipitation by tannins opens up an interesting field of speculation. Moreover, it seems probable that the phenomenon described as precipitation is one of interaction (either physical or chemical) of alkaloid and tannin; and is not due to precipitation of unchanged alkaloid hydrochlorides

through supersaturation. This is supported by the fact that intensity of precipitation does not vary from 1 per cent. to 10 per cent. solutions. If the reaction were merely one of supersaturation, those alkaloids showing opalescence in 1 per cent. solution might be expected to give a definite precipitate, or, at least, a decided increase in opalescence in 10 per cent. solution.

The assumption that the alkaloids are general reagents for the tannins has evidently to be modified.

BIOCHEMICAL LABORATORY,
BRISTOL UNIVERSITY.

DISCUSSION.

The PRESIDENT said that this was an interesting piece of work done under the Analytical Investigation Scheme. It was a valuable contribution because it systematically examined and, to a certain extent, refuted a statement which was largely and generally accepted about the precipitation of all alkaloids. The only thing which struck him was that all the precipitations were made in neutral solutions, and there were some alkaloids, he thought, which were not precipitated in neutral solution, but were in acid solution ; he suggested that the work might possibly be extended to determine the precipitability in various acid solutions.

The Refraction of Milks Low in Solids-not-fat.

BY G. D. ELSDON, B.Sc., F.I.C., AND J. R. STUBBS, M.Sc., F.I.C.

(*Read at the Meeting of the Northern Section, March* 1, 1929.)

ABOUT two years ago (ANALYST, **1927, 52, 193**) we gave an account of our experience with the refractometer as a weapon for the detection of added water in milk, and later (*id.*, **1928, 53, 150**) gave some supplementary results supporting the conclusions at which we had arrived as the result of our previous work.

It has been stated that the method is very useful and reliable in cases of the type:—Fat, 3·2; solids-not-fat, 8·2; ash, 0·7 per cent.; refraction of copper serum, 38·5 at 20° C.

We have already dealt with one aspect of this claim in a recent paper (*Chem. and Ind.*, 1928, **47**, 1145), and we now offer the result of a further year's observations in continuation of our work on this subject.

During the year 1928 we have examined some 2850 samples of milk, and have observed the refraction of a considerable number of these. This number has included all those in which the solids-not-fat were less than 8·5 per cent.

It is interesting to examine the figures we have obtained on the analysis of the whole of the milks received during the year having less than 8·5 per cent. of solids-not-fat. A few milks with solids-not-fat of 8·5 per cent. have been included, and in every case where a corresponding "appeal-to-cow" sample has

been obtained the figures for this are given for comparison. The "acidity" is the number of c.c. of 0·1 *N* sodium hydroxide solution per 10 c.c. of milk.

	Original Sample.				"Appeal-to-Cow" Sample.			
Date.	Fat.	Acidity.	Solids-not-fat.	η	η	Solids-not-fat.	Acidity.	Fat.
Jan. 10	3·3	2·2	8·0	36·6	37·7	8·6	2·6	3·7
,, 27	2·4	1·6	7·0	33·8	37·2	8·4	2·0	3·2
Feb. 7	3·6	2·0	8·2	36·9	—	—	—	—
,,	3·8	1·9	8·0	36·5	37·7	8·7	2·2	3·5
,,	2·3	2·0	7·9	35·7	38·2	8·6	2·2	3·7
,, 17	3·1	2·1	8·0	36·3	38·4	8·9	2·6	3·2
,, 23	3·3	1·9	8·1	36·3	38·2	9·1	2·1	3·3
,, 29	2·4	1·7	7·8	35·6	37·4	8·4	2·0	2·1*
Mar. 6	2·8	1·7	8·1	36·7	37·4	8·6	2·1	2·8
,, 15	3·0	1·7	7·4	35·0	37·8	8·5	2·4	3·3
,, 21	2·6	2·8	7·5	35·5	37·4	8·4	2·3	3·1
	3·6	2·5	7·8	36·5	37·6	8·4	2·9	4·0
April 11	3·2	1·9	8·3	37·5	—	—	—	—
	3·3	2·0	8·2	37·4	—	—	—	—
,, 12	3·4	2·2	8·1	35·7	38·8	9·0	2·9	4·0
,, 23	2·4	1·6	7·5	34·4	37·9	8·8	2·1	3·7
,, 24	3·7	2·2	8·3	36·8	37·7	8·5	2·5	2·6
	2·6	2·2	8·5	36·6	37·5	8·6	2·2	2·5
	4·0	2·1	7·9	36·1	38·0	8·6	6·0	3·2
May 7	3·4	—	8·2	36·5	—	—	—	—
June 21	2·9	2·1	8·3	36·4	—	—	—	—
July 18	3·0	2·1	8·3	36·6	37·6	8·7	2·1	3·0
,, 23	3·2	1·8	8·0	36·5	37·9	8·5	1·8	3·7
,, 24	3·1	1·6	8·0	36·3	38·8	8·7	5·8	3·3
	2·8	1·6	8·4	36·8	—	8·4	—	2·7
,, 26	2·8	1·6	7·6	35·0	38·7	9·0	2·0	4·1
,, 27	3·5	1·8	8·3	37·0	—	—	—	—
	4·0	1·7	8·1	36·9	—	—	—	—
Aug. 16	3·4	1·7	8·2	36·9	—	—	—	—
	3·0	1·8	8·3	37·1	—	—	—	—
,, 28	3·2	1·9	8·1	36·8	37·6	8·7	2·2	3·3
Sept. 14	3·5	1·6	7·8	35·3	38·8	9·2	2·0	3·6
,, 21	3·0	1·8	8·6	36·5	—	—	—	—
,, 26	3·0	1·5	7·6	34·8	38·2	9·0	2·2	3·7
Oct. 5	3·5	1·8	8·1	35·8	—	—	—	—
	4·0	1·7	8·5	37·0	—	—	—	—
,, 8	3·2	2·0	7·1	34·3	37·0	8·3	2·2	3·8
,, 9	3·6	2·0	7·8	36·3	36·0	7·8	1·6	3·6*
Nov. 14	4·0	1·7	8·3	36·7	—	—	—	—
,, 15	3·2	1·9	6·4	32·5	37·8	8·7	2·0	4·5
	3·0	2·8	6·8	33·4	37·8	8·9	2·3	3·6
	3·4	2·0	8·2	36·3	—	—	—	—
	3·2	2·0	8·4	37·0	—	—	—	—
,, 23	3·9	6·2	8·2	38·3	—	—	—	—
	3·2	4·5	7·8	36·6	39·0	8·5	5·5	4·9
	3·3	3·8	8·1	37·4	39·0	9·1	3·0	3·9
	2·8	4·1	8·2	37·9	39·0	9·0	2·8	3·5
Dec. 13	2·2	2·1	8·1	36·6	—	—	—	—
,, 21	4·0	1·9	8·0	35·9	—	—	—	—
	3·5	2·0	8·2	36·3	—	—	—	—
	4·2	2·1	8·1	36·4	—	—	—	—

* One cow.

From an examination of this table it will be seen that in every case (except two, which are dealt with below) a low solids-not-fat corresponds with a low refraction. This means one of two things—or possibly a combination of both.

Either all the low solids-not-fat are due to watering or to the fact that milks naturally low in solids-not-fat do not give a normal refraction of 38 or more. It must be emphasised that our own results were obtained from 2850 samples of mixed milks, and that we have now examined in all well over 8000 samples with similar results.

The figures for the first and fourth samples received on November 23 agree very closely with those given in paragraph two above. Objection may, therefore, be taken that these samples do not conform to our contention that a milk having a low solids-not-fat will have a low refraction. Such a conclusion would, however, be quite unjustifiable, for these samples actually illustrate quite well the point we tried to establish in our paper in *Chem. and Ind.* (*loc. cit.*). Both samples had become sour before examination, and the high refractions are to be attributed to this fact. No "appeal-to-cow" sample was taken in connection with the first sample, but, in the case of the fourth, watering was certainly proved by this means.

In those cases where "appeal-to-cow" samples were taken, the refraction of these was greater than that of the original sample in every case except one. This was found to be milk from an individual cow, and all the figures agreed well with those of the original sample, proving that no water had been added and that a milk naturally low in solids-not-fat may give a low refraction.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

XIV. A New Method for the Separation of Small Quantities of Tantalum and Niobium from Titanium.

By W. R. SCHOELLER, Ph.D., and C. JAHN.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, May 1, 1929.)

This Section marks a further advance in our quest for a reliable quantitative method for separating titanium from tantalum and niobium. In Section IX (Analyst, 1927, 625), Schoeller and Deering have shown that, when a solution of the tartaric complexes of the metallic acids is boiled with a large excess of mineral acid, the earth acids are precipitated, whilst titanic salt remains in solution ("tartaric hydrolysis method"). The separation is approximate, because the earth acids are not quite quantitatively precipitated and the precipitate occludes titania. Now, whereas the titania content of the earth-acid precipitate can be

reduced to a very small figure by one or two repetitions of the procedure, the recovery of the small amount of earth acid that accompanies the titania into the filtrates is a much more arduous problem. The task we set ourselves was to discover a method capable of recovering a small amount of earth acid in presence of a relatively large quantity of titania; in other words, a supplementary procedure that would resolve into its constituents the titania fraction from the tartaric hydrolysis process.

What seemed the most promising point of attack was to utilise the ready formation of a soluble titanium complex of one of the aromatic hydroxy-compounds (*cf.* Hauser and Lewite, *Ber.*, 1912, **45**, 2481). Muller attempted a quantitative separation by means of salicylic acid, but his method, involving a number of re-treatments, was proved by Schoeller and Deering (*loc. cit.*) to result in loss of earth acid at each repetition of the procedure. After many fruitless attempts with a variety of reagents (see final paragraph) we eventually modified and greatly improved a method (the principle of which was evolved by one of us in 1923) hereafter designated as the "oxalate-salicylate method."

TARTARIC HYDROLYSIS METHOD FOR SMALL QUANTITIES OF EARTH ACIDS.—Before describing the oxalate-salicylate method we will give some necessary details of tartaric hydrolysis on a small scale, as this forms the final stage of our new process.

Procedure.—The oxides are fused with 0·25 grm. of potassium bisulphate in silica, and the product dissolved in a hot strong solution of 0·25 grm. of tartaric acid. The liquid is transferred to, or filtered into, a small beaker, and treated while boiling with 5 c.c. of strong nitric acid, the total bulk being 25 to 30 c.c. After 5 to 15 minutes' boiling, the beaker is allowed to stand a few hours, the precipitate mixed with a little filter pulp, collected, washed with dilute ammonium nitrate solution, ignited wet, and weighed as $(Ta, Nb)_2O_5$. The results are given below (initial bulk, 30 c.c.):

Exp.	M_2O_5 taken.	TiO_2 added.	Precipitate formed:	M_2O_5 recovered.
	Grm.	Grm.		Grm.
1	0·0009	—	after 15 minutes' boiling	0·0003
2	0·0030	—	,, 3–4 ,, ,,	0·0030
3	0·0060	—	,, 2 ,, ,,	0·0060
4	0·0090	—	at once	0·0090
5	0·0010	0·0050	after 15 minutes' boiling	0·0004
6	0·0035	0·0054	,, 4 ,, ,,	0·0030
7	0·0060	0·0055	,, 2 ,, ,,	0·0059
8	0·0090	0·0057	at once	0·0091

As shown by these tests, the quantitative recovery of the earth acids is practicable, provided the dilution is not excessive: serious negative errors occurred only in Exps. 1 and 5, with an initial M_2O_5 concentration of 0·03 mgrm. per c.c. A minimum concentration of 0·1 mgrm. should be aimed at; on the other hand, the concentration should not be too high (*e.g.* above 1 mgrm. per c.c.), because

precipitation would be too sudden, the precipitate being more slimy than flocculent and occluding titania, if present (*v. infra*, Exp. 17). The recovered M_2O_5 must be fused with bisulphate, and the melt dissolved in a warmed mixture of hydrogen peroxide and sulphuric acid; any yellow tint is matched against that produced by a standard titanium solution, and the necessary correction made.

When carried out with the precautions here given, tartaric hydrolysis on a small scale is an eminently satisfactory precipitation reaction of the earth acids: a fraction of a mgrm. is readily recovered from a bulk of about 2 c.c. by boiling with 1 c.c. of nitric acid. At the same time, a good separation from titania is achieved.

THE OXALATE-SALICYLATE METHOD.—When a solution containing the oxalates of titanium and ammonium and a small quantity of oxalo-earth acids is treated with an excess of sodium salicylate, the characteristic orange colour of the salicylic titanium complex is produced. If now the oxalic ion is removed from the solution by addition of calcium chloride, the bulky oxalate precipitate carries down the earth acids whilst the titanium complex remains unaffected. The precipitation of the earth acids not being quantitative, the titania is recovered from the filtrate and the treatment repeated. The oxalate precipitates are dissolved in hydrochloric acid and the oxalic acid destroyed by permanganate; the earth acids are precipitated from the acid solution as tannin complexes. The ignited precipitates are finally submitted to tartaric hydrolysis (*v. supra*).

THE SEPARATION: *Precipitation of the Major Earth-acid Fraction.*—The mixed oxides (0·2 to 0·3 grm.) are brought into solution by fusion with potassium bisulphate (2 grms.) in a silica crucible and treatment of the fusion product with a hot solution of ammonium oxalate (2·0 grms.) in an 800 c.c. beaker. Five grms. of sodium salicylate B.P. are dissolved in hot water and added to the boiling solution (bulk, 250 c.c.), which is stirred and precipitated with a small excess of a 20 per cent. calcium chloride solution, added gradually in small portions. The solution must not be allowed to cool at this stage or to stand any length of time, otherwise orange crystals of the titanium compound may contaminate the oxalate precipitate. Hence, after five minutes' settling on a boiling water-bath, the clear supernatant liquid is tested for complete precipitation with a little calcium chloride solution, and filtered at once by suction on an 11 cm. Postlip filter, supported by a platinum cone. The precipitate is well washed with a hot 2 per cent. sodium salicylate solution till the washings are colourless. The hot filtrate and washings are transferred to another 800 c.c. beaker and evaporated. The oxalate precipitate is returned to the precipitation vessel; the paper is washed with hot water, then with 40 to 50 c.c. of hydrochloric acid (1:1), and discarded. The hydrochloric solution is boiled, the precipitate readily dissolving, and cautiously treated with excess of strong permanganate solution. When the transient brown colour of the higher manganese compounds has been discharged by further boiling, the liquid is diluted to 300 or 350 c.c. with boiling water, treated with one grm. of tannin in strong, freshly-made solution, boiled for another ten minutes, and the precipitate

left to settle completely on the water-bath. The above manipulations occupy two hours or less. The precipitate, TP^1, is collected on a loose filter, washed with 2 per cent. ammonium chloride solution containing a little tannin, and ignited wet in a porcelain crucible.

Precipitation of the Minor Earth-acid Fraction.—When the bulk of the orange salicylic filtrate has been reduced to about 150 c.c., the hot liquid is treated with pure, solid ammonium chloride (about 40 grms.) until a copious yellow crystalline precipitate forms, and left to itself overnight. A large part of the coloured titanium compound crystallises out during evaporation, but the addition of ammonium chloride (an observation made and placed at our disposal by our collaborator, Mr. A. R. Powell) depresses its solubility so much that the titania is almost wholly precipitated. The crystals are filtered off by suction and washed with saturated ammonium chloride solution; they are returned to the beaker, which is set aside after the filter has been washed with hot water and discarded.

The mother liquor from the salicylate crystals is boiled with 5 grms. of ammonium acetate and 0·5 grm. of tannin till the small precipitate flocculates. This is filtered off, washed with 2 per cent. ammonium chloride-tannin solution, ignited wet, and fused with a very little bisulphate. The product is dissolved in a hot solution of ammonium oxalate (2·0 grms.), and the liquid rinsed into the beaker containing the yellow titanium crystals. On being heated, they readily dissolve, leaving a white residue of calcium oxalate, which is not filtered off. Sodium salicylate (5 grms.) is now added, the volume made up to 250 c.c., and the boiling liquid precipitated with calcium chloride, etc., exactly as before: the final product is the ignited tannin precipitate TP^2.

The second salicylate filtrate and washings should be perfectly clear; any turbidity is filtered off, washed, and added to the oxalate precipitate.

Treatment of the Tannin Precipitates.—The precipitate TP^1 is fused with bisulphate (0·25 grm.) for tartaric hydrolysis. The tartaric solution, before precipitation with nitric acid, is filtered through a small filter for the elimination of any insoluble (siliceous) particles. The washed filter is incinerated and the ash added to the ignited precipitate TP^2, which is evaporated in a tiny platinum cup (made of foil) with one drop of sulphuric and a little hydrofluoric acid. The dry residue is fused with a small particle of bisulphate, dissolved in about one c.c. of tartaric acid solution, and the clear liquid added to the solution of TP^1. This is boiled in suitable bulk (TP^1 may be weighed as a guide) with nitric acid, etc., as described before. The precipitate, HP, is ignited and weighed, and finally tested colorimetrically for titania, which is often entirely absent; $(HP - TiO_2) = (Ta,Nb)_2O_5$.

Results of Test Analyses.—In the table below we give the results of ten consecutive test analyses of mixtures the M_2O_5 content of which (with the exception of Nos. 9 and 10) was unknown to the operator. In Exps. 9 to 12 the minor fraction was not recovered; in the six subsequent tests we weighed the major and

minor fractions separately (*HP*[1] and *HP*[2]), so as to furnish data for a critical discussion of the method.

Exp.	M_2O_5 taken.	TiO_2 added.	*HP*[1].	*HP*[2].	TiO_2 in *HP*.	M_2O_5 found.	M_2O_5 error: observed.	M_2O_5 error: corrected.[3]
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
Ta9	0·0148	0·2036	0·0126	—	0·0005	0·0121	−0·0027	−0·0002
Nb10	0·0159	0·2024	0·0135	—	0·0002	0·0133	−0·0026	−0·0001
Ta11	0·0116	0·2000	0·0089	—	nil	0·0089	−0·0027	−0·0002
Nb12	0·0104	0·2006	0·0069[1]	—	nil	0·0069	−0·0035[1]	−0·0010[1]
Ta13	0·0128	0·2040	0·0096	0·0005	nil	0·0101	−0·0027	−0·0002
Nb14	0·0150	0·2004	0·0118	nil	trace	0·0118	−0·0032	−0·0007
EA15	0·0338	0·1500	0·0291	0·0008	0·0001	0·0298	−0·0040	−0·0005
,, 16	0·0065	0·2513	0·0052	nil	nil	0·0052	−0·0013	+0·0002
,, 17	0·0240	0·2026	0·0209	0·0006	0·0005[2]	0·0210	−0·0030	0·0000
,, 18	0·0034	0·2506	0·0016	0·0004	nil	0·0020	−0·0014	+0·0001

[1] Filtrate from oxalate precipitate slightly cloudy: low result.
[2] TiO_2 co-precipitated in tartaric hydrolysis because solution was too concentrated (*v. supra*).
[3] For correction factor, see below.

At first sight the observed errors may appear sufficiently high to excite adverse comment; but we would remind our critics that we are at grips with a problem of such complexity as to have defeated the efforts of its ablest investigators, so that an alternative method is not yet available (see Sections IX, *loc. cit.*, and XII, ANALYST, 1928, 470). That being understood, we may explain that the error can be reduced to very small proportions by the application of an empirical correction factor, an expedient recognised as legitimate even in much simpler cases. Now the observed errors are consistently negative. We ascribe them to incomplete earth-acid flocculation at the calcium oxalate precipitation stage, the amount remaining in colloidal suspension being determined to a greater extent by the volume of solution than by the absolute quantity of earth acid present: the figures show that the loss does not increase proportionally with the weight taken, the absolute error being low but the relative error high in the case of small quantities (Exps. 16, 18), and *vice versa* (Exps. 15, 17). We propose the following corrections:

M_2O_5 found,	<0·0060 grm.:	add 0·0015 grm.
,, ,,	0·0060 to 0·0100 grm.:	,, 0·0020 ,,
,, ,,	0·0100 ,, 0·0160 ,, :	,, 0·0025 ,,
,, ,,	0·0160 ,, 0·0260 ,, :	,, 0·0030 ,,
,, ,,	>0·0260 grm.:	,, 0·0035 ,,

When these are applied, we get within the limits of experimental error (see table), Exp. 12 being disregarded as not having proceeded smoothly. For the present we confine the application of the method to a maximum quantity of 0·04 grm. M_2O_5. For larger quantities the tartaric hydrolysis method is available: this is followed up by the present procedure applied to the titania fraction, so that, in all cases, the final earth-acid error is limited to that incurred and allowed for in the oxalate-salicylate method. Its chief merit is, that it furnishes an earth-acid product so low in titania that it permits of the subsequent separation of tantalum from niobium by tannin (Section XI, ANALYST, 1928, 265). There is

no appreciable difference in the behaviour of tantalum and niobium in the oxalate-salicylate method (Exps. 9 to 14), hence the earth-acid correction is apportioned between the two elements according to the ratio ascertained by the tannin method.

Only one more observation is needful, namely, some comment on the poor earth-acid recovery in HP^2, as compared to the amount not precipitated in HP^1. Thus, in Exp. 15, the recovery of 0·0008 grm. HP^2 from 0·0047 grm. is disappointing, seeing that Exp. 18 yielded 0·0016 grm. HP^1, out of 0·0034 grm. taken. So far we are at a loss for an adequate explanation, but hope to return to the matter in due course as we are continuing our researches. These have, as their next object, the full quantitative separation of tantalum, niobium, and titanium in various proportions by a combination of the published methods.

In the tartaric hydrolysis process the same cause of error (incomplete flocculation) operates as in the oxalate-salicylate method: for "all the net earth-acid results show a negative error" when the operation is carried out in a bulk of 300c.c. (Section IX); on the other hand, the error is inappreciable in small volumes of solution (this Section).

We have not investigated the composition of the salicylic titanium complex formed in our separation process, beyond ascertaining that it is not simply titanium salicylate, but the sodium salt of a complex titanylsalicylic acid. It crystallises in glittering orange oblique prisms soluble in water or alcohol; the salt appears capable of reacting with the excess calcium chloride, part of the sodium being replaced by calcium. The exact constitution of the compound is of less analytical importance than the fact that this is another instance of a fairly successful separation procedure based on the formation of a stable crystalloidal compound, in accordance with the principles laid down in the preamble to Section VI (ANALYST, **1926**, **51**, 613).

UNSUCCESSFUL SEPARATION SCHEMES.—We think it useful to record as briefly as possible, without numerical data, the schemes which, in our hands, proved abortive.

A. Employing Salicylic Acid.—(1) On further investigation, procedure E, Section IX, Part I (*loc. cit.*)—salicylate extraction of a mixed ammonia precipitate—did not lead to an improved separation.—(2) The salicylate method of Dittrich and Freund for the separation of titanium from zirconium (*Z. anorg. Chem.*, **1907**, **56**, 344) was applied, but unsuccessfully, to the recovery of small quantities of earth acids in admixture with much titania.—(3) We vainly attempted a separation by endeavouring to take advantage of the solubility of the salicylic titanium complex in alcohol.

B. Employing other Reagents.—(1) Pyrocatechol: we confirmed the observation of Rosenheim and Sorge (*Ber.*, **1920**, **53**, 937) that precipitated titanic acid is directly soluble in a boiling ammoniacal pyrocatechol solution, but were unable to utilise this remarkable reaction for separation purposes.—(2) Sodium peroxide:

we were led to experiment with the metallic per-acids, in alkaline as well as in acid solution, but without any success.—(3) Precipitation of sodium tantalate and niobate from tartrate solution: like the separation of tungsten from the earth acids (Sect. VIII, ANALYST, 1927, **52**, 511), this scheme is based on the insolubility of sodium tantalate and niobate. After fusion of the oxides with potassium carbonate and solution in tartaric and a little nitric acid, the liquid was treated with sodium hydroxide and solid sodium nitrate. The earth acids were precipitated as crystalline sodium salts fairly free from titania, but the precipitation was far from quantitative and had to be completed by boiling with an excess of nitric acid: hence this procedure is more complicated and less effective than direct tartaric hydrolysis.—(4) Citric hydrolysis: the operations are exactly the same as in tartaric hydrolysis, but citric is used instead of tartaric acid. This gave very incomplete earth-acid precipitation, as the citric complexes have greater stability than those of other organic hydroxy-compounds. Here again, tartaric hydrolysis is the better method.

SUMMARY.—A new method is described for the separation of small quantities of earth acids from large amounts of titania. The solution, containing the oxalates of titanium and ammonium and the oxalo-earth acids, is treated with sodium salicylate, whereby the titania becomes converted into a stable crystalloidal sodium titanylsalicylate. The hot solution is then precipitated with calcium chloride, the bulky precipitate carrying down the earth acids. They are recovered by solution of the precipitate in hydrochloric acid, destruction of the oxalic acid with permanganate, and precipitation with tannin. The tannin precipitate is purified by fusion with bisulphate, solution in tartaric acid, and boiling with excess of nitric acid in very small bulk. The soluble titania fraction is again submitted to the above procedure, after having been precipitated by evaporation and saturation with ammonium chloride of the filtrate from the oxalate precipitate. The errors are consistently negative, a few mgrms. of earth acid escaping precipitation; but serviceable results are secured by the application of an empirical correction. The final pentoxide precipitate is free, or practically free, from titania.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
ALDGATE, LONDON, E.C.3.

Potassium Cyanate as a Reagent for the Detection of Cobalt.

By B. J. F. DORRINGTON, B.Sc., A.K.C., and
A. M. WARD, B.Sc., Ph.D., A.I.C.

(*Read at the Meeting, April* 3, 1929.)

Ammonium thiocyanate has long been used as a reagent for the detection of cobalt in the presence of nickel (Vogel, *Ber.*, 1879, **12**, 2314; Treadwell, *Z. anorg. Chem.*, 1901, **26**, 105; see also Treadwell and Hall, *Analytical Chemistry*, Vol. I, 4th ed., pp. 182–3; p. 184). Complications arise if iron is present, due to the intense blood-red colour of ferric thiocyanate. These difficulties may in some measure be overcome if concentrated ammonium acetate and tartaric acid solutions are added to prevent the formation of coloured iron derivatives, or the iron may be removed by the addition of sodium carbonate solution, or of sodium thiosulphate.

The use of potassium cyanate, instead of potassium or ammonium thiocyanates, seems never to have been suggested, although the cyanate appears to present marked advantages over the thiocyanate method. Iron and nickel do not give coloured complexes with this reagent, whilst the deep blue colour of the cobalt complex formed with potassium cyanate is quite as intense as that obtained with ammonium thiocyanate.

The test was carried out in all cases by adding measured volumes of aqueous solutions of cobalt nitrate (iron and nickel free) to 2 c.c. of an alcoholic solution of potassium cyanate (prepared by shaking sufficient potassium cyanate with absolute alcohol at room temperature so that some of the solid remained undissolved; the filtered solution thus prepared contained 3·8 grm. of potassium cyanate per litre). This procedure is much more convenient to carry out than the shaking of the aqueous solution with amyl alcohol and ether, as in the ammonium thiocyanate test. The following table shows the results of adding volumes of molar cobalt nitrate solution (column one) to 2 c.c. of the alcoholic solution of potassium cyanate :

Vol. added. c.c.	Colour.
0·3	Deep royal blue, with reddish tinge.
0·2	,, ,, ,, ,, ,, ,,
0·1	Deep royal blue diminishing in intensity.
0·05	
0·04	
0·02	
0·01	Pale blue.

A precipitate was present in each case in diminishing quantity (probably potassium nitrate). The reddish tinge in the first two cases is doubtless due to the cobalt nitrate being present in excess. No change took place on allowing the solutions

to stand overnight, except that the reddish tinge in the first case appeared more marked. These experiments were repeated with tenth molar and one-hundredth molar cobalt nitrate solutions; but even with 0·01 c.c. of one-hundredth molar cobalt nitrate solution, corresponding to 6×10^{-6} grm. of cobalt ion, a very pale blue colour was obtained, which was none the less quite definite. The test is much more delicate when carried out as above than when made in aqueous solution. The gradual addition of water to the solutions containing the cobalt complex in the above tests caused the blue colour to weaken, and in each case the addition of 3–4 c.c. of water destroyed it. (*Cf.* Schneider, *Ber.*, 1895, **38**, 1540, who used cobalt acetate, added to an alcoholic solution containing potassium cyanate, as a test for cyanate in the presence of cyanide.)

INFLUENCE OF NICKEL.—With molar nickel sulphate solution (free from iron and cobalt) the addition of diminishing quantities of this solution (0·3 c.c. —> 0·01 c.c.) to 2 c.c. of alcoholic potassium cyanate caused a pale green precipitate to form immediately in diminishing quantity, as the series descended. The supernatant liquid was colourless. Similar results were obtained when tenth molar nickel sulphate solution was used. The results for mixed cobalt and nickel solutions are given below:

	c.c.		
$M/20$ $Co(NO_3)_2$ + $M/20$ $NiSO_4$	0·04	Distinct blue colour.	Precipitates as described in following set.
	0·02	,, ,, ,,	
	0·01	Pale blue colour.	
$M/40$ $Co(NO_3)_2$ + $M/40$ $NiSO_4$	Volumes added 0·3 c.c. —> 0·01 c.c.		

The colour of the first solution (0·3 c.c.) was deep blue, and a greenish-white flocculent precipitate formed immediately. The intensity of the colour, also the amount of the precipitate, diminished as the series was passed down, but the colour was quite pronounced in the last tube. The addition of 0·1 c.c. of $M/200$ $Co(NO_3)_2$+$M/2$ $NiSO_4$ caused a definite blue-green colour, and the colour persisted in the filtered solution. As little as 0·3 mgrm. of cobalt ion may thus be detected in the presence of one hundred times as much nickel ion. The presence of still greater relative amounts of nickel does not invalidate the test, as shown by the following experiment:—A tenth of 1 c.c. of a warm solution of $5M$ nickel sulphate and $M/200$ cobalt nitrate was added to 8 c.c. of the cyanate reagent. A greenish-white precipitate rapidly settled, and the solution was then concentrated to half its bulk by boiling, and filtered. A little solid potassium cyanate was added to the filtrate, which was then concentrated to approximately 2 c.c., and filtered. A clear blue solution was obtained. A blank experiment with nickel sulphate alone gave a colourless, but slightly turbid, solution. One part of cobalt in the presence of one thousand parts of nickel was thus detected.

The test can accordingly be applied for the detection of cobalt in the presence of nickel in the usual scheme of qualitative analysis by adding ammonia to the solution obtained after dissolving the mixed cobalt and nickel sulphides until the solution is faintly alkaline, and then adding one drop of this solution to 2 c.c. of

alcoholic potassium cyanate solution. A blue coloration, resembling cuprammonium solutions in appearance, shows the presence of cobalt.

INFLUENCE OF FERRIC IRON.—The results were as follows for ferric chloride solution ($M/2$):

Vol. added. c.c.	Result. At once.	Result. After standing overnight.
0·3	Clear orange-brown solution.	No change.
0·1	Turbid orange-brown solution.	Precipitate settled.
0·05	More turbid orange-brown solution.	,, ,,
0·02	Turbid light brown solution.	Precipitate settled and solution almost colourless.

Iron was, however, completely removed from solution as follows:—0·1 c.c. of $M/2$ ferric chloride was added to 2 c.c. of alcoholic potassium cyanate, and the solution was boiled and filtered. A small amount of iron remained in solution. A further 2 c.c. of cyanate were added, and the liquid re-boiled and filtered, when a colourless solution was obtained. With $M/10$ ferric chloride solution, added in the same quantities as above, the immediate colour effects and precipitations were as above, but were less pronounced; precipitation was practically complete in each case after standing overnight. With $M/100$ ferric chloride solution, the solutions varied from pale brown to colourless (for 0·02 c.c. of solution). The colour of the alcoholic solution of potassium cyanate after adding the ferric chloride solution was a slightly deeper brown than that of the aqueous ferric chloride used. After standing overnight the solutions which were filtered from the brown precipitates were colourless. The results for a solution containing $M/10$ ferric chloride and $M/10$ cobalt nitrate are given below :

Vol. added. c.c.	Immediate result.
0·3	Brownish-green solution.
0·2	Olive-green solution.
0·1	Blue-green solution; intensity of colour diminishing, but still quite definite in the last solution.
0·05	
0·03	
0·02	
0·01	

After standing overnight the ferric salt had precipitated completely in each tube, leaving a blue solution, the depth of the colour diminishing as the series was passed down. Thus, although the brown colour due to the ferric salt masks the blue colour of the cobalt complex to some extent, the colour change is none the less quite definite and distinctive, and is even more decisive if the solutions are allowed to stand. Experiments with $M/2$ ferric chloride and $M/200$ cobalt nitrate solution gave a conclusive test for cobalt as follows:—

On adding 0·1 c.c. of the solution to 2 c.c. of cyanate reagent an orange-brown solution was obtained. Boiling and filtering removed most of the iron, but the solution was still orange-brown. A further 2 c.c. of cyanate were added, the

solution re-boiled and filtered, when a pale blue-green solution resulted. Similar treatment of ferric chloride alone (see above) gave a colourless solution. The presence of one part of cobalt in 100 parts of iron was thus detected, but this does not represent by any means the limit of the relative amounts of iron and cobalt, for the presence of one part of cobalt in the presence of 1600 parts of iron was shown quite definitely as follows:—

An addition of 0·1 c.c. of a solution of 8 *M* ferric chloride and *M*/200 cobalt nitrate was made to 8 c.c. of cyanate reagent. A reddish-brown precipitate at once separated, and the solution was then boiled and filtered with the aid of the pump, a few crystals of potassium cyanate added, the solution reboiled and concentrated to about half bulk, and again filtered, when a greenish-brown solution resulted. Further crystals of potassium cyanate were added, the solution concentrated by boiling to about 2 c.c., when a pale blue-green solution resulted, showing the presence of cobalt. A blank experiment was carried out as described above, 0·1 c.c. of 8 *M* ferric chloride solution being used, when a colourless solution showing no trace of blue-green colour resulted. Some cobalt was doubtless removed during the elimination of iron from solution, for the colour of the resulting solution was not so deep as for 0·1 c.c. of *M*/200 cobalt nitrate solution alone.

Reactions with other Metals.—Experiments were carried out on the addition of all the common cations (1 drop of 2*N* solution) to 2 c.c. of alcoholic potassium cyanate reagent. Only in the cases of ferric and of copper salts were coloured solutions obtained. Detailed experiments showed that a blue coloration, due presumably to the cupric ion, results on adding cupric salt solutions to the cyanate, but all the copper is precipitated on standing, a colourless solution being obtained. Experiments were made with mixed cobalt and copper solutions; and, although the colour of the cobalt complex was obtained after the liquid had stood sufficiently long for all the copper salt to be precipitated, a better method of procedure would be to remove the copper in acid solution by means of hydrogen sulphide, boil off the excess of hydrogen sulphide, and then add one drop of the solution remaining to 2 c.c. of the cyanate reagent. In this way 0·01 c.c. of a solution containing *M*/2 $CuSO_4$ and *M*/2 $Co(NO_3)_2$ gave a deep blue coloration with the cyanate reagent, whilst 0·09 c.c. of *M*/2 $CuSO_4$ and *M*/200 $Co(NO_3)_2$ gave a perfectly definite test for cobalt.

Coloured solutions or precipitates were also obtained on adding the following solutions to the cyanate reagent in the usual way:—

Uranium acetate:	Yellow solution and almost immediate separation of pale yellow precipitate.
Titanous chloride:	Purple turbidity, completely precipitated on standing a short time.
Gold chloride:	Lemon yellow solution, no precipitate.
Vanadium sulphate:	Deep greenish brown flocculent precipitate.

In the case of vanadium sulphate it would appear that a vanadium complex is precipitated, since the addition of vanadium sulphate solution to alcohol alone

gives only a very slight precipitate and a brown coloured solution. A blue coloration is also obtained by adding two drops of ammonium molybdate to 2 c.c. of potassium cyanate reagent to which one drop of reagent solution of stannous chloride has been added. It seems unlikely, however, that such a combination of circumstances would arise to cause complication in carrying out the cobalt test. Tungsten has a similar effect.

PREPARATION OF THE COBALT COMPLEX.—The blue complex formed by cobaltous salts with potassium cyanate was prepared by Blomstrand (*J. prakt. Chem.*, 1871, [2], **3**, 221) by dissolving cobaltous oxide in glacial acetic acid and adding potassium cyanate, presumably using concentrated solutions. A deep blue crystalline solid separated on allowing the solution to stand overnight (Blomstrand found K=25·86, Co=19·34 per cent.; $K_2Co(CNO)_4$ requires K=25·57, Co=19·35 per cent.). Blomstrand's method of preparation was repeated; a crop of crystals was rapidly separated by cooling the mixed solutions in an ice-salt freezing mixture; these were filtered with the aid of the pump, dissolved in a small quantity of cold water, cooled in the freezing mixture, and the crop of crystals, which separated at once, filtered off and air-dried. The crystals retained a very slight smell of acetic acid, and were therefore purified by dissolving in acetone, followed by precipitation by means of ether.

ANALYSES.—A quantity of 0·2028 grm. of substance gave 0·21 grm. of $CoSO_4+K_2SO_4$ (by Main Smith's method, *J. Soc. Chem. Ind.*, 1925, **44**, 539T; *Chem. News*, 1926, **132**, 65), whence Co+K=44·55 per cent.; calc. for $K_2Co(CNO)_4$, Co+K=44·92 per cent. Nitrogen was determined by Kjeldahl's method (Found 17·8, 18·0 per cent.; calc. 18·36 per cent.) Several determinations of carbon were carried out by decomposing the complex with dilute sulphuric acid, and by weighing the carbon dioxide evolved. The results in all cases were low (found, for example, C=13·47, 12·93, 14·59 per cent.; calc., C=15·74 per cent.). It therefore seems certain that the complex does not undergo complete conversion into carbonate when decomposed in this way, and that other substances, possibly urea, are formed (*cf.* O. and I. Masson, *Z. physikal. Chem.*, 1910, **70**, 290, who consider that potassium cyanate decomposes in aqueous solution in accordance with the equation $4KCNO+6H_2O \longrightarrow 2K_2CO_3+(NH_4)_2CO_3+CO(NH_2)_2$).

PREPARATION OF POTASSIUM COBALTOCYANATE.—The preparation of potassium cobaltocyanate was also carried out by mixing solutions of potassium cyanate (30 grms. in 40 c.c. of water) and cobaltous sulphate (30 grms. in 40 c.c. of water) at room temperature. A very deep blue solution was obtained, and a precipitate (12·5 grms.) separated at once, whilst a further 2·5 grms. deposited after standing a short time. These crops probably are mainly potassium sulphate. Deep blue crops were obtained by the addition first of alcohol and then of ether to the solution remaining (total weight of product 24 grms.). Analyses of these crops gave variable results, but purification by extraction with acetone, followed by precipitation with ether, yielded pure potassium cobaltocyanate (found Co+K=44·69 per cent.).

SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C.3.

DISCUSSION.

The PRESIDENT congratulated the authors on discovering, or, at any rate, adapting, a delicate and distinctive test for cobalt. With regard to the use of alcohols, since water was so destructive to the delicacy of the test, he would like to enquire whether the small amount of water in industrial methylated spirit would be destructive. Secondly, he would like to know what was the nature of the solution applied; was it a neutral solution?

Dr. DUNN suggested that, as the colour was so clear in this test, it might be possible not only to detect but also to determine cobalt in this way. He congratulated the authors on the clearness with which the test was described.

Dr. WARD, replying, stated that he and his co-worker had not tried the test with industrial methylated spirit, but he thought that the small amount of water present would not decrease the sensitiveness of the test or prevent its being carried out satisfactorily. With regard to the solution used, there was no need to take any special precautions, beyond using the salts dissolved in water. He had made no attempt to put this test on a quantitative footing, but it seemed quite feasible that this might be done.

Official Appointments.

Mr. F. C. BULLOCK, B.Sc., F.I.C., as Public Analyst for the County Borough of Leicester (to date from July 1st, 1929).

Mr. ERIC VOELCKER, A.R.C.S., F.I.C., as Additional Public Analyst for the County of Northampton (June 7th, 1929).

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.

RICE HUSKS IN BRAN AND SHARPS.

A SAMPLE of bran and a sample of sharps examined by the writer a few months ago were both found to be adulterated with rice husks.

Although a prosecution arising from the presence of rice husks in sharps is on record (ANALYST, **1924**, **49**, 429), the use of this substance as an adulterant of bran and sharps is not, to the knowledge of the writer, a common practice.

It seemed, however, that the present note might prove useful, in view of the fact that, since the Fertilisers and Feeding Stuffs' Act (1926) became operative, the number of samples of mill offals submitted for analysis has increased considerably.

Rice husks are light brown in colour; the outer surfaces have a dull appearance, whilst the inner surfaces are shiny. They are very stiff and hard, and are characterised by their rough, harsh nature. This harshness is easily detected by scraping the outer surface with a needle.

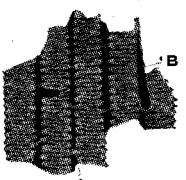
In bran, the particles of rice husk may be large enough for them to be recognised by the above characteristics; but in sharps, where the particles are much smaller, their detection by the naked eye is usually impossible.

Samples of bran or sharps, which contain a considerable proportion of rice husks, will indicate this adulteration in their fibre content; whereas a normal bran has a fibre content of 7 to 10 per cent., and a normal sharps of 4·5 to 6·5 per cent., rice husks contain about 40 per cent. of fibre. It must be remembered, however, that it is possible to obtain samples of sharps with a fibre content of about 3·5 per cent., and such samples, even after an adulteration with 10 per cent. rice husks, would have a fibre content within the normal range.

The structure of the rice husk is so different, however, from that of the wheat grain, that the detection of rice husk in bran and sharps by microscopical examination is a simple matter.

A little of the suspected sample of bran or sharps is boiled with a solution of chloral hydrate (water 2, chloral hydrate 5 parts), and a drop of the liquid is then placed on a microscope slide, covered with a coverslip, and examined.

Rice husks, which are the glumes and paleae of the fruit, consist of four layers of tissue, *viz.* outer epidermis, fibrous hypoderma, spongy parenchyma, and inner epidermis. It is by the cells of the outer epidermis, which are very characteristic, that the particles of rice husk are recognised. These cells (see Fig.), which are arranged in longitudinal rows, are square in general outline, but their side walls are extremely sinuous. This peculiar sinuous form is very distinctive. The epidermis also bears dagger-shaped hairs, and in places, where these have become detached, hair scars can be seen.



A, hair; B, hair scar. (× about 50.)

Although rice husks, owing to their high silica content, do not yield to clearing treatment for microscopical examination so readily as many seed tissues, they can be resolved into their elements by maceration in Schulze's fluid. This treatment is not necessary for their identification, however, since the outer epidermal cells with the characteristic sinuous form are easily rendered visible by boiling with chloral hydrate solution. (*Cf.* Schröder, ANALYST, 1908, **33**, 280 ; Silberberg, *Id.*, 1923, **48**, 186; *A.O.A.C. Methods*, 1925, p. 122.)

A. J. AMOS.

MESSRS. WOODLANDS LTD.,
CHARLTON GREEN, DOVER, KENT.

A NEW SENSITIVE COLOUR REACTION OF COPPER.*

CERTAIN oxidising agents, when added to very dilute feebly alkaline solutions of a cupric salt containing dimethylglyoxime, produce an intense reddish-violet colour resembling that of permanganate. That produced by sodium hypochlorite or bromine water is rather fugitive, partly due to the sensitiveness of the colour to acid and excess alkali, and to the difficulties of adjusting the P_H value when using these oxidants. Ammonium persulphate produces a weak reddish colour, but on addition of a trace of silver nitrate, an immediate development of the intense permanganate colour occurs, especially when pyridine is used as the means of obtaining slight alkalinity. As a result of many experiments carried out to determine the concentration of reagents most favourable for the reaction, the following

* Communication from the Research Department, Woolwich.

is proposed as a method for the detection and determination of traces of copper in solution:—

The solution, which must be free from chloride, is neutralised and rendered very faintly acid (1 drop of dilute (1:3) sulphuric acid in excess). It is placed in a 100 c.c. Nessler glass, made up to volume, and 1 grm. of ammonium persulphate is dissolved in the solution; 1 c.c. of saturated alcoholic dimethylglyoxime, 0·5 c.c. of a 0·5 per cent. solution of silver nitrate, and 2 c.c. of 10 per cent. aqueous pyridine are added, and the whole is stirred. The colour may be compared colorimetrically by running a standard solution of copper sulphate (1 c.c.= 0·00001 grm. of Cu) into 100 c.c. of a solution containing the same amounts of reagents. The comparison should be carried out without undue delay, as the colour shows some tendency to fade on standing. Where slight opalescence, due to traces of chloride (impurity in the reagents) appears, it is permissible to discharge it by adding a little more than the specified amount of pyridine. As little as 0·01 mgrm. of copper yields a distinct reddish-violet colour, the method is not suitable for determining more than 0·1 mgrm. One part of copper can be readily detected in 10,000,000 parts of water. Comparative tests at 100 c.c. volume with the xanthate and ferrocyanide methods have shown that this reaction is somewhat more sensitive than the former, and from five to ten times as sensitive as the latter. Small amounts of certain other heavy metals give yellowish or brown colorations under the conditions of the test, but the reddish-violet colour appears to be specific for copper.

S. G. Clarke.
B. Jones.

MEASUREMENT OF THE STRENGTH OF SUNLIGHT.

The note by H. H. Bagnall (Analyst, 1929, 101) is an interesting and valuable practical contribution to the study of the comparison of the ultra-violet radiations reaching town and countryside. Whilst we believe that the figures give an indication of the quantities of ultra-violet radiation present at the various places, and also that the conclusions drawn are sound, yet it appears to us that the method is open to some theoretical criticism.

(1) The reactions should be conducted in quartz and not in glass vessels. Ordinary window glass (2 mm. thick) absorbs all radiations shorter than 320 $\mu\mu$, and bottle glass probably absorbs still more of the ultra-violet spectrum. This means that the range 295 $\mu\mu$ to 320 $\mu\mu$ present in brilliant summer sunlight does not reach the test solution, and it is the radiations within this range that produce many of the most beneficial therapeutic and bactericidal effects. Hence the ratio of effective ultra-violet radiation at, say, Regent Road and Nab Top Sanatorium, may be very different from that indicated by the ratio 744·5:885·8. The wave-lengths shorter than 320 $\mu\mu$, probably only present at the Sanatorium, never reach the solution, and hence are not detected by the test. We also suggest the use of a spherical vessel, thereby eliminating the irregular effect of the stopper.

(2) It should be known exactly which wave-lengths accomplish the decomposition of the potassium iodide. We ourselves have used for the examination of mercury-vapour lamps a solution of uranium acetate and oxalic acid in water (*J. Soc. Chem. Ind.*, 1925, **44**, 453T; *British J. Actinotherapy*, 1927, January and May), which is sensitive to ultra-violet radiation shorter than 320 $\mu\mu$. Such information considerably increases the value of any actinometer test.

(3) The colour of the potassium iodide solution becomes orange as the iodine is liberated. We question whether one unit of ultra-violet radiation will liberate the same quantity of iodine from the nearly colourless potassium iodide solution

as it will liberate from an orange-coloured mixture of solutions of iodine and potassium iodide. If it does not, then the quantity of iodine liberated is not directly proportional to the amount of ultra-violet radiation incident on the solution.

J. EWART MOSS.
ARTHUR W. KNAPP.

BOURNVILLE, BIRMINGHAM.

THE DETECTION OF THE PROHIBITED VEGETABLE AND COAL TAR COLOURS IN FOODSTUFFS.

Two of the supplementary tests, as described in THE ANALYST, 1927, **52**, 587, have been found to be unsatisfactory.

Test 16 is fallacious. The violet colour stated to be given by naphthol yellow is not due to that dye. It is given by any alkaline solution which has been shaken with ether and from which the ether has not been completely removed by boiling. The original tests were carried out on alkaline extracts obtained as detailed in the scheme on page 589. The solutions were all boiled to remove ether, but in the case of the naphthol yellow solution the removal must have been incomplete. Test 16 should be deleted.

Test 17 has been found to give a green fluorescence in certain instances with the reagents alone. This has been traced to the excess permanganate oxidising part of the resorcinol, possibly to a dibasic aliphatic acid, which then combines with the remaining resorcinol to form a fluorescing substance. In order to avoid this possibility it is necessary to reduce the excess permanganate after the oxidation. The test has therefore been modified and has been made more delicate as follows:

"To 1 vol. of the alkaline solution add ½ vol. of concentrated sulphuric acid and a little solid permanganate. Boil for 1 minute and then decolorise the solution by the addition, drop by drop, of sodium sulphite solution. Add a few crystals of resorcinol and boil gently until the water has evaporated and fuming starts. Pour into water and extract once with ether. Wash the separated ether with water, discarding the latter, and then shake the ether with a little dilute ammonia solution." Naphthol yellow is the only one of the prohibited colours which gives a green fluorescing colour in the lower layer.

J. R. NICHOLLS.

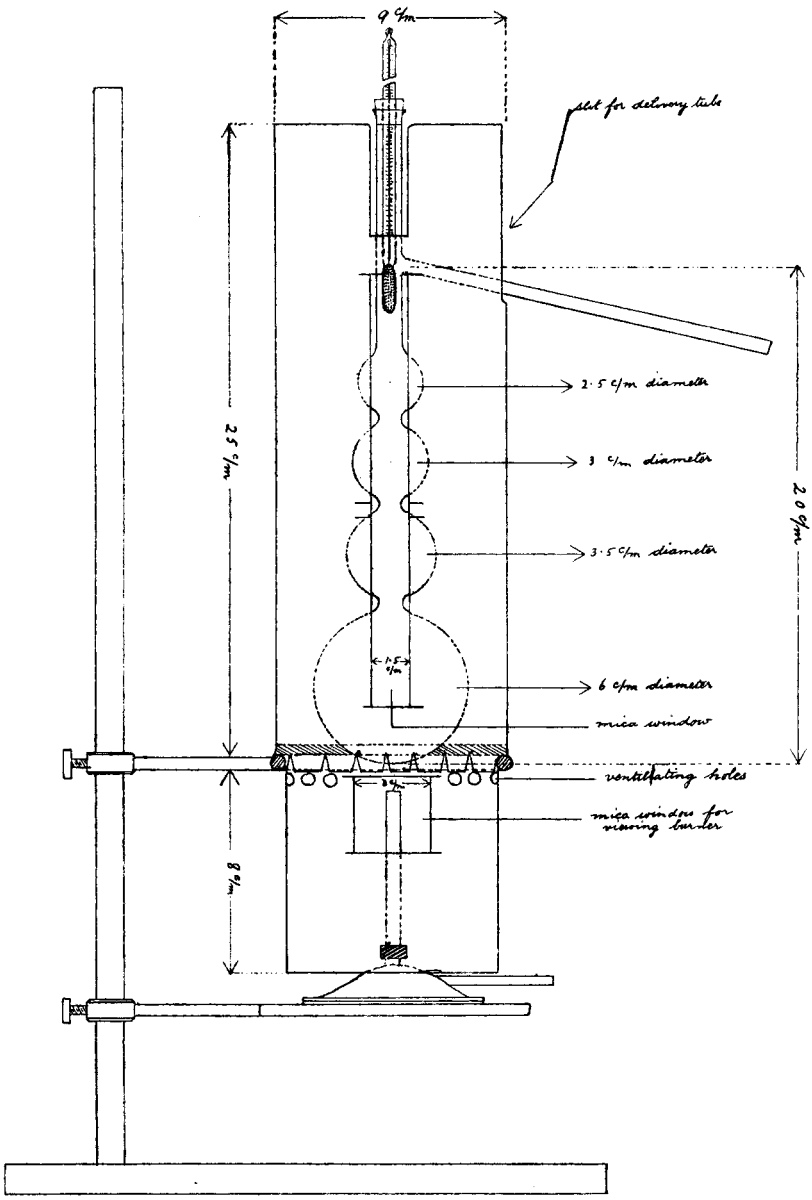
GOVERNMENT LABORATORY, W.C.2.

Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods.

PHYSICAL CONSTANTS (2).

THE Sub-Committee make the following recommendations:—

FREEZING AND MELTING POINTS.—The apparatus recommended consists of a stout-walled glass test tube, 125 mm. × 30 mm. (inside measurements), fitted into a wide-mouthed jar or bottle of about 500 c.c. capacity, by means of a bored cork; and an inner test tube, 100 mm. × 21 mm., fitted into the larger tube also by means



Standard Distillation Apparatus for Essential Oils.

of a bored cork. The thermometer used should be readable to 1/5th of a degree, and should have a diameter about 5 mm. or 6 mm., and the length of the bulb should be between 15 mm. and 20 mm.

Freezing Points: Method of Procedure.—In order to obtain a preliminary indication, a few c.c. of the oil are cooled in a small test tube and stirred with the thermometer until solidification takes place; the temperature is noted and the tube of solidified oil set aside in a cool place. The outer container of the apparatus is then filled with water (or brine) at a temperature about 5 degrees lower than that indicated above, and the larger outer tube fitted in its place. Into the inner tube 10 c.c. of the oil are placed, the thermometer inserted, and the tube and oil cooled to the temperature indicated in the preliminary test. The tube and contents are now inserted in the apparatus, and the temperature allowed to fall a further 1 or 2 degrees. The oil is then seeded with a trace of the previously solidified oil and stirred with the thermometer until solidification takes place.

The highest temperature reached is taken as the freezing point.

Melting Points.—After the determination of the freezing point the inner and outer tubes are removed together from the water jacket and the temperature allowed to rise slowly, the oil being stirred continuously with the thermometer until the liquid becomes "clear." If necessary, the temperature may be raised by holding the outer tube in the hand, or, in the case of a low melting point, the water jacket may be used to prevent too rapid a rise in temperature. The temperature at which the liquid becomes "clear" is taken as the melting point.

A few crystals usually remain unmelted at this point, and the appearance of these crystals furnishes a sharp indication of the melting point. Until the liquid becomes "clear" the unmelted crystals are dull, but at the "clearing" point they suddenly become glistening.

When testing oils of low melting point, the result may be vitiated by the presence of moisture, which will prevent the "clearing" of the oil. An oil which is originally clear below its melting point may become cloudy from atmospheric moisture condensed in the tube during the cooling. In such cases the oils must be dried with anhydrous sodium sulphate.

Determinations on a number of aniseed and fennel oils by members of this Sub-Committee showed variations not exceeding $\pm 0{\cdot}2^\circ$ C.

Otto of Rose.—In the case of otto of rose the freezing point cannot be determined by the standard method, as there is no definite rise in temperature on solidification. The following method is recommended in the case of this oil:—The prescribed apparatus is used, the outer container having been filled with water about 10 degrees below the freezing point, as indicated by a preliminary test. The oil is placed in the inner tube and stirred gently with the thermometer until crystals begin to separate. This point is taken as the freezing point. The temperature is allowed to fall a further 2 degrees, and then the two tubes together are removed from the water jacket. The temperature is allowed to rise slowly, stirring gently the while until the liquid becomes free from all but a few characteristic glistening crystals. This point is taken as the melting point. Tests may differ by as much as $\pm 0{\cdot}5^\circ$ C.

BOILING POINTS.—The Sub-Committee consider that uniformity can be attained only by the use of standardised apparatus and conditions, and the following are recommended:—

(1) The shape and dimensions of the distilling flask are to be in accordance with the accompanying sketch.

(2) The flask is to be supported on a sheet of asbestos board through which a hole 4 cm. in diameter has been cut. Both flask and burner are to be protected from draughts by a screen, in accordance with the sketch.

(3) A plain glass tube, 1 to 1·2 cm. bore, and 65 cm. long, is to be used as an air condenser. The lower end is to be bent down and drawn out slightly. The condenser is to be connected with the delivery tube of the flask by means of a bored cork.

(4) The amount taken for the test is to be 50 c.c.

(5) The flask is to be heated by a naked flame, and a fragment of broken porcelain or pipe stem added to promote even ebullition.

(6) The rate of distillation is to be 50 to 70 drops per minute.

(7) The thermometer is to be either of the short-stem type or else corrected r emergent column, and the top of the bulb is to be level with the bottom side of the delivery tube.

(8) The temperature is to be corrected:—

(i) For variation in barometric pressure

$\pm$ 1° C. for each 20 mm. variant from 760 mm.

(ii) For emergent column by the formula:—

$$T = t + 0{\cdot}000143\ (t - t^1)N$$

where T = corrected temperature, t = observed temperature, t^1 = mean temperature of emergent column, and N = length of emergent column in scale degrees.

Thermometers.—The accuracy of the thermometers used in these determinations is to be checked by comparison with N.P.L. standard instruments.

(*Signed*),

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J. Parry, C. Edward Sage, W. H. Simmons.

T. Tusting Cocking (Honorary Secretary).

April 26, 1929.

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.

TINNED "THICK" CREAM.

On May 3rd, a firm of grocers was summoned at Norwich for selling a tin of thick cream which was not of the quality demanded.

Mr. C. G. Ransome Williams, for the prosecution, said that the inspector bought a 6d. tin of thick cream, which, on analysis, was found to contain only 21·04 per cent. of milk fat, whereas it should have contained at least 35 per cent.; for commercial cream generally contained 50 per cent.

Mr. Gerald Dodson, for the defence, said that the importance of this matter lay in the fact that since the Regulations of 1926–1927 had prohibited the addition of all preservatives to cream a new industry had grown up. According to the old regulations it was recognised that cream containing 35 per cent. of milk fat might be preserved with boric acid, but these regulations referred exclusively to dairy cream. There was no legal standard for cream, and although the Ministry of Health had power to fix a standard, they had never done so, and this 35 per cent. mentioned in the certificate of the Public Analyst had never been fixed by law. It was therefore for the Court to decide whether the cream bought by the inspector was purchased to his prejudice. The Court had to perform the task which the Ministry might have done for it, and to decide what standard there should be for tinned cream, as opposed to dairy cream. In order to sterilise cream effectively it must not contain more than 25 per cent. of milk fat, and if more fat was present the article would not be merchantable.

The Magistrates dismissed the case.

ORANGE QUININE WINE.

A FIRM of druggists was summoned by the Bethnal Green Borough Council, on April 23rd, at Old Street Police Court, for selling orange quinine wine deficient in quinine to the extent of 17 per cent. and containing no orange wine.

The inspector said that when he unwrapped the bottle he saw that there was a label with the words "Orange Quinine Tonic."

The manager of the defendant company said that the cost of the quinine wine of the British Pharmacopoeia was 3s. 4d. per bottle, and that of the orange and quinine tonic 1s. 6d. per bottle. When some of his customers asked for orange quinine wine he found that they meant his tonic.

Mr. Glyn Jones submitted that, apart from anything else, the label on the bottle was sufficient, and there could be no conviction.

The Magistrate (Mr. Clarke Hall) said that it was clear that there had been a misunderstanding between the parties, and no intention on the part of the defendants to defraud. The summons would be dismissed.

A similar summons was brought against another firm of druggists, for selling orange quinine wine 17 per cent. deficient in quinine, and entirely deficient in orange wine, since it contained no alcohol.

The solicitor for the defence said that in view of the fact that orange quinine wine was not mentioned in the British Pharmacopoeia, the inspector's agent asked for something which did not exist, and the druggist had to do the best he could in the circumstances.

This summons was also dismissed.

NON-ALCOHOLIC RAISIN WINE.

ON April 23 a Bermondsey manufacturer answered an adjourned summons, at the Lambeth Police Court, of having given a false warranty to the effect that certain raisin wine supplied by him to an East Dulwich tradesman complied with the provisions of the Food and Drugs Act.

Mr. E. A. Pinchin, Public Analyst, certified that the contents of the bottle, which was labelled "British Non-Alcoholic Raisin Wine," consisted of a solution of sugar in water coloured with an aniline dye.

Mr. Fox-Andrews, for the defence, contended that if the article was of the recognised commercial standard, the fact that it contained no raisins did not constitute an offence.

Mr. E. J. Parry, F.I.C., said that the article made by the defendant was of the usual commercial standard in this country of non-alcoholic raisin wine. It was the only substance that could correctly be so described. In his analysis the Public Analyst had taken no notice of the flavouring.

Mr. Hodgson, barrister, appearing for the prosecution, said that the Public Analyst thought that there might be a trace of flavouring in the article. The real question in the case was what was expected by the public. Anyone asking for raisin wine would expect to find some raisin juice in it.

The Magistrate (Mr. Sandbach), giving judgment, said that it was agreed that all the ingredients found in British wines were present in this wine. He came to the conclusion that, from the commercial point of view, the article was what the consumer expected to get, and the summons would be dismissed.

An application for costs was refused.

The National Physical Laboratory.

REPORT FOR THE YEAR 1928.*

THE Report is on the same lines as last year (ANALYST, 1928, **53**, 340–341), dealing with the work of the physics, electricity, metrology, engineering, metallurgy, aerodynamics depts., and the William Froude National Tank. A special report is included on the units and standards of measurement used at the Laboratory. This defines the units, international and British Imperial, with information as to the primary standards preserved and maintained at the Laboratory, and in a few special cases particulars of secondary standards. (For information on the proposed International Temperature Scale see ANALYST, 1929, 292.)

Physics Dept.—Work has been begun on the specific heat of gases at high temperatures and high pressures; the latent heat and specific volume of sulphur dioxide are being redetermined in order to supply more reliable data for the construction of entropy-temperature diagrams for various refrigerants; the study of the laws governing the efficiency of water sprays for moistening and cooling air has been begun, and the moisture absorbing properties of silica gel are being investigated. A number of investigations have been undertaken in the industrial applications of *X*-ray crystal analysis (including the examination of tungsten magnet steels and the effect of heat treatment). The selective orientation of the crystals obtained in rolling aluminium is largely influenced by the previous history of the specimen. The International unit for *X*-ray measurement of dosage is now agreed upon as "the quantity of *X*-radiation which, when the secondary electrons are fully utilised, and the wall effect of the chamber is avoided, produces, in 1 c.c. of atmospheric air at 0° C. and 76 cm. mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation current."

Metrology Department.—The preliminary work on pivots and jewels in instruments shows that rust is formed on the end of the pivot as it rotates in contact with the jewel, and does not appear when the pivot remains stationary, and increases

* Obtainable at Adastral House, Kingsway, W.C.2. Price 7s. 6d.

as the number of revolutions increase and concurrently with the torque due to friction. *Glass Volumetric Apparatus and Hydrometers.*—The Dairy Research Committee have drawn up a memorandum and questionnaire dealing with co-ordination of specifications of glassware used for testing milk and milk products which has been sent to all governments of the Empire interested. A "strain-viewer" has been made for examining colorimetric glassware, consisting of a polarising mirror on the base of a wooden box reflecting a beam of polarised light through a ground glass window in the side of the box, the apparatus in front of the window being examined through a Nicol prism on a vertical brass column. During 1928, 5099 pieces of glass-ware were tested, an increase of 50 per cent. over the previous year. A draft specification for a series of hydrometers small enough to be used with 50 ml. samples has been prepared; 645 (against 679 for 1927) hydrometers were tested during 1928.

AERODYNAMICS DEPARTMENT.—The construction of the new Compressed Air Tunnel has been begun.

METALLURGY DEPARTMENT.—A great deal of work has been done on the preparation of pure iron and chromium; the physical structure of metals and alloys, including study by means of *X*-rays, has continued to receive attention; a considerable number of single crystals of various metals has been produced, having diameters up to 1¼ in.; exploratory work on new alloys, particularly of those in which aluminium is the predominant metal, has been undertaken, and alloys for high temperature work have been prepared.

D. G. H.

Parliamentary Notes.

ARTIFICIAL CREAM ACT, 1929.*

AN ACT TO REGULATE THE SALE AND MANUFACTURE OF ARTIFICIAL CREAM. [10*th May*, 1929.]

BE it enacted by the King's most Excellent Majesty, by and with the advice and consent of the Lords Spiritual and Temporal, and Commons, in this present Parliament assembled, and by the authority of the same, as follows:—

1.—(1) No person shall sell or offer or expose for sale for human consumption under a description or designation including the word "cream" any substance purporting to be cream or artificial cream as defined in this Act unless—

(*a*) the substance is cream as defined in this Act, or

(*b*) where the substance is artificial cream as defined in this Act, the word "cream" is immediately preceded by the word "artificial."

(2) Every receptacle used for the conveyance of artificial cream for sale for human consumption, or containing artificial cream at any time when it is exposed for such sale, shall have the words "artificial cream" printed in large and legible type either on the receptacle itself or on a label securely attached thereto.

(3) If any person contravenes any of the provisions of this section, he shall be guilty of an offence against this Act.

2.—(1) Artificial cream shall not be manufactured, sold or exposed or kept for sale for human consumption except at premises registered with the Food and Drugs Authority:

* [19 & 20 Geo. 5.] [Ch. 32.] To be obtained from H.M. Stationery Office, price 2d. net.

Provided that this requirement shall not apply—

(*a*) to the manufacture of artificial cream, by any person solely for his domestic purposes; or

(*b*) to the manufacture on any premises of artificial cream for use in the preparation on those premises of some other article of food; or

(*c*) to the sale, exposure or keeping for sale of artificial cream on any premises where it is not supplied otherwise than in the properly closed and unopened receptacles in which it was delivered to those premises.

(2) The Food and Drugs Authority shall keep a register of premises under this section, and shall on application being made by the owner or occupier of any premises enter the premises in the register and shall from time to time revise the register as occasion may require.

(3) Any officer of the Food and Drugs Authority duly authorised in that behalf by the authority may at all reasonable times enter and inspect any premises registered with the authority under this section.

(4) If a justice of the peace is satisfied by information on oath that there is reasonable ground for supposing that any unregistered premises are being used for the manufacture of artificial cream contrary to the provisions of this section, he may grant a search warrant authorising any such officer as aforesaid to enter and inspect the premises and to search for and seize any machine suitable for use in the manufacture of artificial cream.

(5) If any person uses any unregistered premises for the manufacture or sale of artificial cream in contravention of this section, or obstructs any such officer as aforesaid in the execution of his powers under this section, or fails to give any such officer all reasonable assistance in his power, or to furnish him with any information he may reasonably require, he shall be guilty of an offence against this Act.

3. Such of the provisions of the Public Health Acts, 1875 to 1926 (or, in London, the Public Health (London) Acts, 1891 to 1926), and the Milk and Dairies (Consolidation) Act, 1915, and of any order or regulation made under any of those Acts, as relate to cream (other than those relating to registration) shall apply to artificial cream.

4. It shall be the duty of every Food and Drugs Authority to enforce the provisions of this Act, and any expenses incurred by the authority for that purpose shall be defrayed as expenses under the Food and Drugs (Adulteration) Act, 1928:

Provided that this section shall not apply to such of the provisions of any Act, order or regulation applied by this Act as are enforceable by any other authority.

5.—(1) If any person commits an offence against this Act, he shall be liable on summary conviction to a fine not exceeding, in the case of a first offence, five pounds, in the case of a second or subsequent offence, fifty pounds, and in any case where the offence is a continuing offence, to a further fine not exceeding forty shillings for each day during which the offence continues.

(2) For the purposes of proceedings under this Act—

(*a*) where artificial cream is sold or offered, exposed or kept for sale, it shall be presumed to be sold or offered, exposed or kept for sale for human consumption unless the contrary is proved;

(*b*) where any article having the composition of cream or artificial cream is sold or exposed or kept for sale on premises registered under this Act, it shall be presumed to be artificial cream unless the contrary is proved.

(3) The provisions of subsection (6) of section twenty-seven and of sections twenty-nine and thirty of the Food and Drugs (Adulteration) Act, 1928, relating to offences and warranties under that Act, as set out with the appropriate modifications in the Schedule to this Act, are hereby incorporated with this Act and shall apply to proceedings under this Act.

6. In this Act—

"Food and Drugs Authority" has the same meaning as in the Food and Drugs (Adulteration) Act, 1928;

"Cream" means that portion of natural milk rich in milk fat which has been separated by skimming or otherwise;

"Artificial cream" means an article of food resembling cream and containing no ingredient which is not derived from milk except water or any ingredient or material which by virtue of the proviso to subsection (2) of section two of the Food and Drugs (Adulteration) Act, 1928, may lawfully be contained in an article sold as cream.

7. This Act shall apply to Scotland subject to the following modifications:—

(*a*) The following section shall be substituted for section three—

Such of the provisions of the Milk and Dairies (Scotland) Act, 1914, and of any order, regulation or byelaw made under that Act as relate to cream (other than those relating to registration) shall apply to artificial cream:

(*b*) The expression "defendant" shall mean "respondent," and the expression "information" shall mean "complaint."

8.—(1) This Act may be cited as the Artificial Cream Act, 1929.

(2) This Act shall come into operation on the first day of June, nineteen hundred and twenty-nine.

(3) This Act shall not extend to Northern Ireland.

SCHEDULE.

PROVISIONS OF FOOD AND DRUGS (ADULTERATION) ACT, 1928, APPLIED.

1. Where an employer is charged with an offence against this Act, he shall be entitled, upon information duly laid by him, to have any other person whom he charges as the actual offender brought before the court at the time appointed for hearing the charge, and if, after the commission of the offence has been proved, the employer proves to the satisfaction of the court that he had used due diligence to enforce the execution of this Act, and that the said other person had committed the offence in question without his knowledge, consent or connivance, the said other person shall be summarily convicted of the offence, and the employer shall be exempt from any penalty.

2. Subject to the provisions of this schedule a defendant shall be discharged from any prosecution under this Act for selling, or offering or exposing for sale artificial cream, if he proves to the satisfaction of the court that he had purchased the article in question as cream, and with a written warranty or invoice to that effect, and that he had no reason to believe at the time of the commission of the alleged offence that the article was not cream and that at that time the article was in the same state as when he purchased it.

3. A warranty or invoice shall only be a defence to proceedings under this Act if—

(*a*) the defendant has within seven days of the service of the summons sent to the prosecutor a copy of the warranty or invoice with a written notice stating that he intends to rely on it and specifying the name and address of the person from whom he received it and has also sent a like notice of his intention to that person; and

(*b*) in the case of a warranty or invoice given by a person resident outside the United Kingdom the defendant proves that he had taken reasonable steps to ascertain, and did in fact believe in the accuracy of the statement contained therein.

4. The person by whom the warranty or invoice is alleged to have been given shall be entitled to appear at the hearing and to give evidence, and the court may, if it thinks fit, adjourn the hearing to enable him to do so.

5. Where the defendant is a servant of the person who purchased the article under a warranty or invoice he shall be entitled to rely on the provisions of this schedule in the same way as his employer would have been entitled to do if he had been the defendant, provided that the servant further proves that he had no reason to believe that the article was not cream.

6. Every person who wilfully applies to an article in any proceedings under this Act a warranty or invoice given in relation to any other article, shall be guilty of an offence against this Act.

7. Every person who, in respect of artificial cream sold by him as principal or agent, gives to the purchaser a false warranty in writing, shall be guilty of an offence against this Act, unless he proves to the satisfaction of the court that when he gave the warranty he had reason to believe that the statements or descriptions contained therein were true.

8. Where the defendant in a prosecution under this Act has been discharged under the provisions of this schedule relating to warranties, any proceedings under this schedule for giving the warranty relied on by the defendant in the prosecution, may be taken as well before a court having jurisdiction in the place where the contravention of this Act took place as before a court having jurisdiction in the place where the warranty was given.

Ministry of Health.

THE Minister has sent the following Circular (No. 989) to the Clerks of Authorities administering the Food and Drugs Acts:—

ARTIFICIAL CREAM ACT, 1929.

SIR,

1. I am directed by the Minister of Health to draw the attention of the Food and Drugs Authority to the Artificial Cream Act, 1929, which will come into operation on the 1st June next. The substance whose sale and manufacture the Act is designed to regulate is a cream substitute which has hitherto been commonly known as reconstituted cream and is usually prepared by emulsifying butter, dried skimmed milk and water. The definition in Section 6 of the Act is however drawn in sufficiently wide terms to include any article of food resembling cream and containing nothing but the ingredients of cream.

2. Sub-section (1) of Section 1 provides that where any substance purporting to be cream or artificial cream is artificial cream, it shall not be sold under a description or designation including the word "cream" unless that word is immediately preceded by the word "artificial." This provision is more specific than that of Section 2 of the Food and Drugs (Adulteration) Act, 1928, and, as the Authority are no doubt aware, the machinery of that Act has generally been considered to be inadequate to prevent the sale of artificial cream as cream, since if due precautions are taken in blending the ingredients of artificial cream an analyst cannot distinguish it from cream.

3. The new Act contains a number of further provisions for facilitating the enforcement of the principal requirement. Under Sub-section (1) of Section 1 receptacles used for conveying artificial cream or for containing it when it is exposed for sale must be labelled with the words "artificial cream" in large and legible type; Section 2 requires that with certain specified exceptions premises where artificial cream is manufactured or sold must be registered with the Authority; and Section 5 (2) (*b*) provides that where an article having the composition of cream or artificial cream is sold on premises so registered it shall be presumed to be artificial cream unless the contrary is proved.

4. This circular will be placed on sale, and further copies may be obtained directly from His Majesty's Stationery Office or through any bookseller. Copies are being sent to the Medical Officer of Health and the Public Analyst.

I am, sir, your obedient servant,

May 24th, 1927. R. B. CROSS (*Assistant Secretary*).

Ministry of Agriculture and Fisheries.

FERTILISERS AND FEEDING STUFFS ACT, 1926.

PROCEDURE UNDER SECTION 13(3).

THE following letter (C.C. 5286) has been sent by the Ministry to the Clerks of Local Authorities administering this Act:—

SIR,

I am directed to inform you that several cases have already arisen in which persons objecting to the certificate of an agricultural analyst in respect of a sample taken under the provisions of the above-mentioned Act, have requested that a part of the sample should be submitted to the Government Chemist for analysis. It seems to be desirable, therefore, in order to obviate delay in similar cases which may arise in the future, that the most convenient procedure for adoption in these cases should be laid before the responsible officers of Local Authorities.

(2) It will be observed that Section 13(3) of the Act provides that:—

> "If the person by or on whose behalf the sample of an article is taken and analysed, or the owner or seller of the article, objects to the certificate of the agricultural analyst, the person objecting thereto shall, on payment of such fee as may be fixed by the Treasury, be entitled to have submitted to the Government Chemist the part of the sample retained by the agricultural analyst and to have that part analysed by him and to receive from him a certificate of the result of his analysis."

(3) In any case where objection is taken to the certificate of the agricultural analyst, arrangements should be made to send to the Government Chemist, as soon as possible, AND BY REGISTERED POST:—

(i) The part of the sample retained by the agricultural analyst in accordance with Section 13(2).

(ii) Copy of the statutory statement or warranty or of the particulars marked on or indicated by a mark applied to the article (see Section 13(4)).

(iii) Copy of the agricultural analyst's certificate, which may be of assistance to the Government Chemist in concentrating attention upon the specific point in dispute.

(iv) The name and address of the person requiring the analysis to be made, and from whom the fee is recoverable.

(4) The address of the Government Chemist is

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.2.

(5) The fee fixed by the Treasury for the analysis of a sample by the Government Chemist is £2 2s. 0d., but it is not necessary for the Local Authority to take any steps to collect this sum.

I am, &c.,

Feb. 27th, 1929. (*Signed*) A. P. A. DOBSON.

United States Department of Agriculture.

CERTIFICATION OF COAL-TAR FOOD COLOURS.*

THE PERMITTED DYES.

Two new colours, Ponceau SX and Sunset Yellow FCF, are hereby added to the list of coal-tar dyes accepted for certification by the department. The following coal-tar dyes are now accepted for certification as described on pages 4 to 6 of Service and Regulatory Announcements, Food and Drug No. 3:

Red shades.—80. Ponceau 3R. 184. Amaranth. 773. Erythrosine, Ponceau SX.

Orange shade.—150. Orange I.

Yellow shades.—10. Naphthol Yellow S.; 640. Tartrazine; 22. Yellow AB.; 61. Yellow OB.; Sunset Yellow FCF.

Green shades.—666. Guinea Green B.; 670. Light Green SF Yellowish; Fast Green FCF.

Blue shade.—1180. Indigotine.

The numbers preceding the names refer to the colours, as listed in the Colour Index published in 1924 by the Society of Dyers and Colourists of England, which gives the composition of these dyes. Names not preceded by numbers are not listed in the Colour Index. The composition of such dyes will be furnished on application to the Food, Drug, and Insecticide Administration.

R. W. DUNLAP,
Acting Secretary of Agriculture.

WASHINGTON, D.C., *April* 2, 1929.

* Service and Regulatory Announcements, Food and Drug No. 3, Supplement No. 1.

A Correction.—We regret that in the May issue (p. 290) the word "tabloids," which should only be applied to the products of Messrs. Burroughs, Wellcome & Co., was inadvertently used for "tablets."—EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Distinction between Pressed and Extracted Cacao Butter. Aufrecht. (*Chem. Ztg.*, 1929, **53**, 318.)—The means by which cacao butter has been separated may be ascertained as follows: 2 grms. of the butter are dissolved in 5 c.c. of chloroform in a dry test-tube, the clear solution obtained being gently mixed with 5 c.c. of fuming hydrochloric acid (1·192; about 37 per cent.). In presence of extracted cacao shell butter, the lower liquid layer turns first pale green, and, after a minute, dark green. When heated at 50° C. for 2 minutes with 2 drops of concentrated nitric acid (1·42), this mixture becomes reddish-brown with a violet tinge, or, in the case of cacao butter extracted from residues, brownish-yellow. After standing for five minutes at 50° C., the colour changes to brownish-violet. With the expressed butter, the mixture remains colourless, both when cold and when heated. This reaction detects an addition of 20–25 per cent. of cacao butter extracted from either shells or residues. No trace of a colour reaction is obtained with ordinary or hardened coconut fat, palm kernel fat, hardened whale oil, vegetable hard butter ("Cocola" and "Kernal"), French vegetable fat ("Banka"), or English hard butter ("Makon").

An even sharper distinction is possible with sulphuric acid. If a solution of 2 grms. of the extracted or residue butter in 5 c.c. of chloroform is treated with 5 drops of sulphuric acid (1·84), the mixture becomes at once deep violet, this changing to brownish-violet after 2 minutes in a water-bath at 50° C. With mixtures of the expressed and extracted butters the colour is pale brown (cold) or deep brownish-violet (50° C.). Pure expressed cacao butter gives a colourless (cold) or a reddish-yellow liquid with a violet tinge (50° C.). Stearin, coconut fat, palm kernel fat, refined Dutch vegetable fat, vegetable hard butter, and hardened fats show no colour reaction. In mixtures of extracted and pressed cacao butter about 10 per cent. of the former is detectable in this way. With mixtures of doubly refined extracted cacao butter with the expressed butter the hydrochloric acid test fails, but the sulphuric acid test detects 20–25 per cent. of the former. When chocolates, etc., are to be examined, the fat is extracted with ether, the filtered ethereal solution evaporated at a low temperature, and the fat dissolved in chloroform and tested as above. T. H. P.

Fachini's Reaction for the Detection of Olive Residue Oils. R. Marcille. (*Ann. Falsif.*, 1929, **22**, 163–166.)—Since Fachini's reaction (ANALYST, 1926, **51**, 416, 636) may give positive results with true olive oils, it cannot be regarded as specific for residue oils. The depth of colouring depends on the quality of the oil, and particularly on the amount of resinous material which may have permeated into the oil, owing to decomposition of the olives before treatment. The reaction is useful for characterising olive oil in mixtures on the assumption that all olive

oils give some colour, but that kernel oils do not, and for deciding if oils of low acidity contain refined oils of inferior quality, without specifying if these are olive residue oils. D. G. H.

Luminescence of a Genuine Dutch Lard in Ultra-Violet Light. A. van Druten. (*Z. Unters. Lebensm.*, 1929, **57**, 60–62.)—Contrary to experience (*cf.* van Raalte, ANALYST, 1929, **54**, 110, and Weiss, *id.*, 178) genuine Dutch lard from pigs slaughtered in the autumn of 1928 gave a bright blue to blue-violet fluorescence in ultra-violet light at 60° C. The intensity was increased after bleaching with 4 per cent. of fuller's earth and 0·25 per cent. of norit, but was decreased after heating at 140° C. In the case of the solid lard the fluorescence appeared on the surface. J. G.

American Safflower Oil. G. S. Jamieson and S. I. Gertler. (*Oil and Fat Ind.*, 1929, **6**, 11–12.)—The characteristics of hot-pressed oil from safflower seed grown in Montana were: Sp. gr., 25°/25° C., 0·9243; n_D^{25}, 1·4744; saponification value, 190·5; unsaponifiable matter, 0·59 per cent.; iodine value (Wijs), 149·1; Reichert-Meissl value, 0·2; Polenske value, 0·1; acetyl value, 12·5; acid value, 5·5; saturated acids (corrected), 5·9; and unsaturated acids (corrected), 87·7 per cent. (iodine value, 156·0). The unsaturated acids consisted of linolenic, 0·16; linolic, 71·82; and oleic 28·02 per cent., and the saturated acids of myristic, 0·7; palmitic, 66·2; stearic, 25·2; arachidic, 6·8; and lignoceric, 1·05 per cent. The oil has a greater drying power than sunflower or soya bean oils, and the press-cake is useful as a cattle food. D. G. H.

Fruits and Seeds of Hydnocarpus Woodii from North Borneo. (*Bull. Imp. Inst.*, 1929, **27**, 12–16.)—The air-dried kernels of these seeds, from fruits received in 1925, contained 7·8 per cent. of moisture, and yielded 57·4 per cent. of oil as a hard, cream-coloured solid having sp. gr. 0·8989 at 100°/15° C., acid value 32·8, saponification value 202·4, iodine value (Hübl, 17 hours) 85·8, unsaponifiable matter 0·5 per cent., n_D^{40}, 1·471; m.pt. 28·5° C., α_D^{20} (in chloroform) +53·1°; the fatty acids had solidification pt, 44·6° C., α_D^{20} (in chloroform) +54·4°. A second sample of kernels, obtained in 1927, contained 8·1 per cent. of moisture, and yielded 55·4 per cent. of oil with α_D^{20} +48·9°, and α_D^{20} of the fatty acids +49·8°, both in chloroform. From the oil, chaulmoogric and hydnocarpic acids were isolated by fractional distillation of the mixed ethyl esters under reduced pressure, followed by repeated crystallisations of the acids. Chaulmoogric acid gave m.pt. 67–68° C., $[\alpha]_D$ +61·9°, iodine value 89·3, percentage of silver in the silver salt 27·2; the corresponding figures for hydnocarpic acid were 58–59° C., +68·2°, 99·5, and 29·8, respectively. Thus the oil of *Hydnocarpus Woodii* seeds contains the glycerides of these two acids, and hence resembles that of *Hydnocarpus Wightiana*, which is largely used for treating cases of leprosy. T. H. P.

Sampling Apples in the Orchard for the Determination of Arsenical Spray Residue. J. W. Barnes. (*Ind. Eng. Chem.*, 1929, **21**, 172–174.)—Separate analyses of 300 apples from 4 trees, showed that the arsenical residue

varied from 0·000 to 0·031 grain of arsenic per apple, the average being 0·011. The range for weight was from 0·004 grain to 0·095 grain per pound of fruit, with an average of 0·031 grain, and the range for area was from 0·05 grain to 1·30 grain per 1000 square inches of area of fruit, the average being 0·45 grain. The trees had received four applications of lead arsenate in a spray of 2 pounds to 50 gallons of water, the last treatment being on July 1st, and the apples were gathered in the middle of October. The following formula is given for calculating the area of an apple from its weight :—$A=0{\cdot}842\ (W)^{2/3}$, where A is the area in sq. inches and W the weight in grms. The results obtained indicate that it is necessary to analyse a sample of about 50 apples picked at random in order to obtain a value with a probable error of 5 per cent. for the mean arsenical residue per pound of fruit. W. P. S.

Preparation of Banana Vinegar. H. von Loesecke. (*Ind. Eng. Chem.*, 1929, **21**, 175–176.)—A banana mash, consisting of the pulp and peel of ripe fruit, was pasteurised at 76° C. for forty-five minutes (without addition of water), cooled, and fermented with *Saccharomyces ellipsoideus*. Fermentation was complete in fourteen days at 20° to 23° C., and the yield of banana cider, containing 9 per cent. of alcohol(by vol.), amounted to 56 per cent. of the weight of fruit taken. The cider was mixed with one-third its volume of strong vinegar and allowed to trickle through a column of beechwood shavings previously boiled in water, dried, and impregnated with vinegar. About fifty hours were required to convert 1 litre of cider into vinegar. Better results were obtained by the Orleans process, in which the cider was mixed with one-fourth its volume of vinegar, put into flasks, and the latter closed with plugs of cottonwool. Acetification was usually complete after seventy-five days at 30° C. The vinegar was finally filtered, clarified with kieselguhr, and pasteurised for one minute at 60° C. The banana vinegar thus prepared had a good colour and pleasing aroma and taste ; it contained from 4 to 7 per cent. of acetic acid. W. P. S.

Manganese in Foodstuffs. C. Newcomb and G. Sankaran. (*Indian J. Med. Res.*, 1929, **16**.)—The proportions of manganese in a large number of substances were determined. They differed widely both in different substances and in samples of the same food. The mean amounts found for some of these include, in mgrms., per kilo. (pts. per million) : Arrowroot, 1 ; barley, 10 ; oatmeal kernel, 348 ; rice, polished 9·5, unpolished 17, husk 130 ; potato starch, 2 ; rice starch, 11 ; cod liver oil, 0 ; sesame oil, 4 ; olive oil, 0 ; betel nut, 39 ; chillies, 14 ; pepper, 64 ; cabbage, 1·3 ; coconut fresh " meat," 15 ; onion, 33 ; tomato, 31 ; cane sugar, 0 ; egg yolk, 2·5 ; egg shell, 17 ; linseed meal, 168 ; milk, 1 ; teas, 115–546 ; and tea infusion, 0·6. In the case of the cereals the manganese is largely lost in the preparation for market. Five grms. or more of food stuff are ashed, any chlorides removed if present to appreciable extent, and if the ash is voluminous and insoluble in dilute nitric acid, it is fused in a nickel vessel with potassium and sodium carbonates and a little potassium nitrate. The fused mass is extracted with water, the extract poured directly into twice the quantity of

dilute nitric acid required for neutralisation, and 6 c.c. of 85 per cent. phosphoric acid, 25 c.c. of silver nitrate (1·5 grm. per litre) and water to make up to about 200 c.c. added, and the whole boiled. Solid ammonium persulphate is then added, little by little, and after a short time the solution will turn pink and the turbidity clear up. The liquid is heated to boiling, another pinch of ammonium persulphate is added, the solution made up to 250 c.c., and the amount of manganese determined by reading against a standard permanganate solution. If there is but little ash, or if it is completely soluble in dilute (1:5) nitric acid, the ash is extracted with dilute nitric acid, any insoluble matter filtered off through a small paper, the paper moistened with a solution of sodium and potassium carbonates, and a little potassium nitrate, dried, burnt on a platinum wire and the bead dissolved in the nitric acid extract. An addition of 2·4 c.c. of phosphoric acid and 10 c.c. of silver nitrate per 100 c.c. of final bulk of solution is made, and the pink colour developed as before. When the amount of permanganate was not less than 0·1 mgrm. per 100 c.c. a Kober's colorimeter was used for the comparison, and with weaker solutions Nessler glasses. D. G. H.

Zinc Contents of the Principal Vegetable Foodstuffs. G. Bertrand and B. Benzon. (*Bull. Soc. Chim.*, 1929, **45**, 168–175.)—To determine zinc in vegetable materials, from 200 grms. for seeds and tegumentary tissues to 1000 or 1500 grms. for leafy parts or parenchymatous organs are heated on a water-bath or in an oven to remove the water, and then carefully ignited in a muffle furnace to destroy the organic matter. The zinc in the residue is then determined by the calcium zincate method. The results obtained for a large number of different materials show that the pulp of fruits and etiolated leaves contain less than 1 mgrm. of zinc per kilo., whilst parenchymatous roots (carrots, etc.), orange pulp, lemon juice, leaves poor in chlorophyll, figs, chestnuts, and grapes contain 1–2 mgrms. Higher proportions appear in organs rich in chlorphyll: thus carrot leaves and lucerne contained 4 mgrms., radish 4·5, cabbage lettuce 4·7, cress 5·6, spinach 6·2, dandelion 9·7. Mature potatoes contained 5, *Boletus edulis* 5·1, bakers' yeast 12·4, garlic 10, onion 13·8, cereals 12 to 19·5, soya beans 20, vetch seeds 23, lentils 24·4, peas 44·5, haricots 52·5, cocoa beans, buckwheat and sweet almonds 10, arachis nuts 16, sunflower seeds 17, dried walnuts 20, pine kernels 55·5, hemp seed 82·6, polished rice 2·5, rice bran 30, white flour (75 per cent. extraction) 6 to 7, wholemeal flour 10 to 15. T. H. P.

Application of the Method of Hagedorn and Jensen to the Determination of Larger Quantities of Reducing Sugars. C. S. Hanes. (*Biochem. J.*, 1929, **23**, 99–106.)—A modification of the method of Hagedorn and Jensen (*Biochem. Z.*, 1923, **135**, 46) is described which enables about 10 times as much reducing sugar as before to be determined. The original method was for the measurement of the reducing sugar in the filtrates from 0·1 c.c. samples of blood, with an upper limit of 0·385 mgrm. of glucose. It consisted in the reduction of potassium ferricyanide, when heated in alkaline solution with certain reducing substances, to ferrocyanide, precipitation of the ferrocyanide as the double potassium zinc salt, and determination of the residual ferricyanide by treatment with excess of

potassium iodide and acidifying. The iodide reduces the ferricyanide quantitatively, and equivalent iodine is liberated according to the equation : $2H_3Fe(CN)_6 + 2HI = 2H_4Fe(CN)_6 + I_2$, and titrated with thiosulphate. Except as regards the volumes and concentrations of the various reagents used, no essential change has been made. The following solutions are needed for the new method :—*Solution A.*—Potassium ferricyanide (8·25 grms.) and anhydrous sodium carbonate (10·6 grms.) are made up to 1 litre with distilled water; this solution must be kept for 2 to 3 days before use, stored in a bottle with an opaque jacket. *Solution B.*—Potassium iodide (12·5 grms.), zinc sulphate (25·0 grms.) and sodium chloride (125·0 grms.) are made up to 500 c.c. with distilled water. Before use this solution must be filtered through 2 thicknesses of filter paper to remove traces of iodine which appear on storing. *Solution C.*—Glacial acetic acid (5 c.c.) diluted to 100 c.c. with distilled water. *Solution D.*—Merck's soluble starch (1 grm.) in about 20 c.c. of cold water is washed into 60 c.c. of boiling water, boiled for 2 minutes, 20 grms. sodium chloride added, the liquid cooled, and made up to 100 c.c. This solution keeps for several months. *Solution E.*—An approximately *N*/75 sodium thiosulphate solution, used in a 10 c.c. burette, graduated in 0·02 c.c. divisions. About 10 litres are made up with boiled-out water (3·33 grms. sodium thiosulphate per litre). This is protected from carbon dioxide by a soda-lime tube, and run through a siphon to the burette. It is standardised against a potassium iodate solution (0·80 grms. in a litre). Five c.c. of iodate solution are pipetted into a boiling tube to which are added 5 c.c. of 2 per cent. potassium iodide solution, and 3 c.c. of solution C. The liberated iodine is titrated with the thiosulphate solution, one drop of solution D added as indicator when the colour is pale yellow, and titration continued to the disappearance of the blue colour. The value for the normality is found from the expression

$$\frac{\text{Grm. } KIO_3 \text{ per litre} \times \text{vol. of pipette (c.c.)}}{35{\cdot}67 \times \text{vol. of thiosulphate required (c.c.)}}$$

and the volume of thiosulphate required is about 9 c.c. The sugar determinations are carried out in boiling-tubes (1 × 7 ins.), with glass bulbs with an inch of tubing left attached as covers. Five c.c. of solution A are pipetted into a boiling-tube, the pipette being allowed to drain a standard time, and then 5 c.c. of the solution whose reducing power is to be determined (or less than 5 c.c. + water to make up to 5 c.c.). A water blank is then prepared—5 c.c. of solution A and 5 c.c. of distilled water. All drops on the sides must be mixed in, and the tubes are then covered with glass bulbs, placed in a boiling water bath, 2 or 3 in. deep, for 15 minutes, and cooled for 3 minutes in cold running water. On adding from a rapid pipette 5 c.c. of solution B a white flocculent precipitate appears and iodine is set free ; 3 c.c. of solution C are added, and the liberated iodine is titrated against the standardised thiosulphate solution in the same boiling tube. The difference between the water blank value (WB), and the reading obtained with the experimental solution (R) gives the thiosulphate equivalent of the ferricyanide reduced by the experimental solution. Standardisation data are given for glucose and maltose, and

shown in a graph. Water blank values need only be determined once or twice a day, and 18 determinations can be done in an hour in batches of 5 or 6. An important advantage over copper methods is pointed out in the fact that variations in the amounts of dissolved oxygen in sugar solutions do not affect the reducing values arrived at by the ferricyanide method. P. H. P.

Beta-anthraquinone-monosulphonic Acid as a Microchemical Reagent for Alkaloids, etc. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, **101**, 196–197.)—Beta-anthraquinone-monosulphonic acid (Beta-A acid) is a general alkaloidal precipitant, although some of the precipitates are not quite insoluble, and in many cases are amorphous. Crystals result from the addition of the following crystalline alkaloidal bases or salts to a 10 per cent. solution of the Beta-A acid: Aniline (sulphate), pink drops then bundles of needles and spears; antipyrine: drops, then sheaves of small needles; atropine sulphate: amorphous, then " bunches " of needles; hydrastinine (hydrochloride): drops, then a micro-crystalline precipitate, at last small rectangular, strongly polarising leaves; nicotine: amorphous, then small aggregates like calcium oxalate; novocaine (hydrochloride): deep orange-red drops, later bunches of needles; tropacaine (hydrochloride)—drops, then bunches of needles. If a small crystal of cinchonine sulphate is placed in a drop of Beta-A acid, bubbles appear on the crystal, but may disappear, and small granules becoming larger or even spherocrystalline masses of needles follow. With salts of quinine and cinchonidine, bubbles only are formed; the forms with quinine sulphate have regular notchings or may be granular; with emetine hydrochloride they are mostly free from notchings. These formations are only produced with the salts, and not usually with the free bases, in consequence of lower solubility. The reaction is considered a " topochemical " one, the typical development of which depends on the drug being from some particular locality.

D. G. H.

Insecticidal Value and Determination of Pyrethrin I and II in *Pyrethrum cinerariaefolium*. I. F. Tattersfield and R. P. Hobson. (*J. Agric. Sci.*, 1929, **19**, 266–296.)—Pyrethrin I and II have been isolated from *Pyrethrum cinerariaefolium*, and, while both are highly toxic (to *Aphis rumicis*), pyrethrin I is about 10 times more so than pyrethrin II. Samples of flowers grown from the same seed on the same soil vary in pyrethrin content within fairly wide limits according to the season. The total amount of the two toxic principles in flowers from 10 localities grown from the seed of the same origin varied in one season from 0·71 to 1·17 per cent. The micro-methods used for determination are adaptations of Staudinger and Harder's macro-methods (*Amer. Acad. Scient. Fennicae A*, 1927, **18**), and the results agreed with observed insecticidal properties. In the acid method 10 grms. of ground flowerheads (50 grms. of stalk) are extracted with petroleum spirit, the solvent evaporated in carbon dioxide, the residue extracted with 4 (stalk 6) lots of 2·5 c.c. of absolute methyl alcohol, and the extracts filtered through cotton wool into a long-necked 100 c.c. flask. The solution is treated with 4 c.c. of *N* sodium hydroxide in methyl alcohol, boiled under a condenser for

6–8 hours, the alcohol removed by warming, the soaps dissolved in-water, and 6 c.c. of *N* sulphuric acid added. The acid liquid is distilled, and after 50 c.c. of distillate have been taken for determination of volatile acid another 100 c.c. are collected. The first 50 c.c. are extracted with 50 c.c. of petroleum spirit, the extracts washed, and after evaporation of the ether the aqueous liquid is titrated with 0·2 *N* sodium hydroxide solution. To the hot residue in the flask (not over 40 c.c.) 0·2 grm. of calcium sulphate is added, and after standing overnight the liquid is filtered into the automatic extractor (illustrated in the text) and extracted with methylated ether for 8 hours, after which 20 c.c. of water are added to the extract and the ether taken off. The aqueous layer is filtered and the dicarboxylic acid titrated with 0·2 *N* sodium hydroxide, of which 1 c.c. is equivalent to 3·36 mgrms. of monocarboxylic acid, 6·6 mgrms. of pyrethrin I, 1·90 mgrms. of dicarboxylic acid or 3·74 mgrms. of pyrethrin II. The semicarbazone method, described in detail, determines the sum of the 2 pyrethrins, and is used as a confirmation of the acid method. The analytical results obtained for a series of pyrethrum samples agreed with their observed insecticidal action on *Aphis rumicis*. Data are not yet sufficient to show significant correlation between size of flower heads and content of poison, or to draw conclusions as to effect of external conditions. D. G. H.

Preservation of Anaesthetic Ether. C. L. Hewer. (*Lancet*, 1929, 770–771.)—The oxidation to which ether is prone may be prevented by treating the ether with carbon dioxide and then storing it in copper containers. When anaesthetic gases are bubbled through ether for long periods, the rate of decomposition of the ether will be greatly diminished if there is an adequate area of copper both above and below the surface level of the liquid. T. H. P.

Colorimetric Determination of Ergot in Flour. F. S. Okoloff. (*Z. Unters. Lebensm.*, 1929, **57**, 63–71.)—For rye flour 10 grms. dried for 1 hour at 110° C., are shaken with a mixture of 500 c.c. of chloroform and 60 c.c. of alcohol (sp. gr. 1·415 to 1·420), and the floating portion filtered off after 1 hour, dried and shaken with 30 c.c. of ether and 1 c.c. of sulphuric acid (1 in 4). The next day the glutinous precipitate is filtered off, the flask and paper washed with ether till 40 c.c. of filtrate are obtained, and 2 c.c. of a saturated solution of sodium bicarbonate added. After the mixture has been shaken, the coloured aqueous layer is transferred to the tube of a Walpole colorimeter, and the colour matched by means of a suitable combination of two standards :—(1) A solution of 0·1 grm. of carmine in a mixture of 5 c.c. of concentrated ammonia and 95 c.c. of water. Portions of from 0·05 to 0·5 c.c. are diluted to 10 c.c., preserved with 2 drops of formalin, and stored in the dark in stoppered tubes. (2) A solution of 0·05 c.c. of methyl orange in 100 c.c. of water, of which 0·2 to 0·5 c.c. portions are diluted to 50 c.c. after the addition of 2 c.c. of 0·1 *N* sodium hydroxide solution. The percentage of ergot is given by the number of c.c. in the carmine solution which exactly matches, the methyl orange solution being used only for the compensation of the yellow colour. If the colour is too intense 0·1 *N* sodium hydroxide solution

is added to the solution, and since 2 c.c. reduces the colour by one-half, the true percentage of ergot is obtained by multiplying the carmine value by half the number of c.c. added. With wheat flour 20 grms. of sample are shaken with 50 c.c. of ether and 5 c.c. of sulphuric acid (1 in 4), filtered after a day, the filtrate diluted to 60 c.c., and the above procedure followed. In this case, however, 0·3, 0·4 and 0·5 per cent. of ergot correspond with 0·45, 0·55 and 0·65 c.c. of carmine solutions, respectively, the smaller quantities being exactly equivalent as before. If the colour is reduced by alkali the ergot percentage must be multiplied by half the number of c.c. used. The methods were shown to be independent of the type or age of the sample, the maximum recorded error for quantities up to 3 per cent. of ergot being 0·2 per cent. J. G.

Biochemical.

Determination of Ergot in Flour by a Serological Method. F. S. Okoloff and I. G. Akimoff. (*Z. Unters. Lebensm.*, 1929, **57**, 72–76.)—An antigen was prepared by the intravenous injection of rabbits with 1·0 to 5·0 c.c. of an extract of ergot from which water-soluble poisons (*e.g.* alkaloids, amines, etc.) were removed by the following treatment:—The de-fatted, dried and powdered ergot was extracted twice with water for 24 hours, the residue dried, and well mixed with physiological salt solution containing 0·5 per cent. of sodium hydroxide solution and chloroform. After 24 hours the mixture was neutralised with a 10 per cent. solution of phosphoric acid and filtered. If the immunisation was extended over a period of 2 months (Raiski) a titre value, for the serum, of 1:20,000 was obtained. The precipitin ring test was then carried out in an agglutination-tube with 2 c.c. of serum and 0·5 c.c. of a filtered solution prepared by extracting 20 grms. of sample with 100 c.c. of physiological salt solution for 24 hours. An ergot content of 0·1 to 0·5 per cent. gave sharply defined rings after incubation for 25 minutes at 37° C., 0·05 per cent. showed more diffuse rings, which were intensified after 35 minutes at room temperature, whilst 0·02 per cent. gave a doubtful ring or an opalescence, and ergot-free flour gave no reaction. Tests for specificity on 11 weeds gave indefinite results, which, however, are not considered to detract from the value of the method. J. G.

Factors affecting the Yield and Quality of Milk. 1. The Age of the Cow. R. R. Kay and H. C. McCandlish. (*J. Agric. Sci.*, 1929, **19**, 342–372.)—As a result of investigating the records of 738 Ayrshire cows for 4380 lactations, it is shown that up to 7 years of age (maturity) milk and butterfat production increase, but there is a tendency to a slightly lower fat percentage with advance of age, probably owing to the fact that, as the milk yield changes, the fat yield does so in the same direction, but at a slower rate. The 3-year-old fat percentage is significantly higher than for other ages, averaging 3·87, falling to 3·76 in the 4-year-old group, and remaining at 3·74–3·77 to 5 to 8 years, and then gradually falling. At 12 and 13 years it averaged 3·23 and 3·45 per cent. The increase of production

with age is partly due to growth of the secretory tissue of the udder and to general body growth, and with maturity is probably more closely associated with high initial production than with persistency of production. Correction factors for age are suggested as follows :—Age 3 years : milk yield 1·16, fat yield 1·13 ; 4 years, 1·12, 1·12 ; 5 years, 1·06, 1·05 ; 6 years, 1·03, 1·03 ; 7 years, 1·00, 1·00. D. G. H.

Determination of Tryptophan by means of *p*-Dimethylaminobenzaldehyde. W. J. Boyd. (*Biochem. J.*, 1929, **23**, 78–82.)—It has been found that errors can arise in the determination of tryptophan in proteins by the method of May and Rose (*J. Biol. Chem.*, 1922, **54**, 213), (1) through unequal illumination of the reacting mixtures, and (2) through the presence of reducing substances such as hydrogen sulphide or aldehydes. For the May and Rose method, 0·1 grm. protein is added to a mixture of 50 c.c. concentrated hydrochloric acid, 50 c.c. water and 1 c.c. of a 5 per cent. solution of *p*-dimethylaminobenzaldehyde in 10 per cent. sulphuric acid. The mixture is incubated for 24 hours at 36° C., and then left for 24 hours or longer at room temperature. When tryptophan is present the solution forms a blue colour, which is compared in a colorimeter with the colour given by caseinogen under the same conditions, and tryptophan is calculated on the assumption that caseinogen contains 1·5 per cent. of tryptophan. As a result of a study of the following factors, (1) effect of reducing substances, (2) effect of oxidising agents, and (3) effect of light, it is shown that the development of the colour is an oxidation process which proceeds slowly in dull light and more rapidly in bright light, and is not nearly complete in a period of 4 weeks in ordinary diffused daylight in the laboratory. The addition of a trace of an oxygen carrier or oxidising agent after hydrolysis of the protein hastens the process. If the oxygen carrier were added at the same time as the reagent, it would alter the aldehyde rapidly before it had time to combine with the tryptophan. Therefore, the best way to avoid the disturbing effects of varying illumination, and of reducing substances, is by the addition of a little sodium nitrite, nitric acid or hydrogen peroxide. In making the test, 3 drops of 0·5 per cent. sodium nitrite solution should be added to the reaction mixture after 24 hours' incubation at 36° C. and 3 days at room temperature, and again after a further 3 days, and the colorimetric comparison should be made next day or later. By this modified method higher values for the tryptophan content of cod-muscle protein and edestin are obtained than by the unmodified method of May and Rose. According to Jones, Gersdorff and Moeller (*J. Biol. Chem.*, 1924, **62**, 183) the tryptophan content of caseinogen is assumed to be 2·2 per cent. P. H. P.

Characterisation of the Anthocyanins and Anthocyanidins by means of their Colour Reactions in Alkaline Solutions. A. Robertson and R. Robinson. (*Biochem. J.*, 1929, **23**, 35–40.)—It has recently been shown by Fear and Nierenstein (*Biochem. J.*, 1928, **22**, 615) that the colour reactions of the anthocyanins, which are indicators, should be examined in solutions of definite P_H. Accordingly the authors have examined the reactions of the anthocyanidins in a

range of buffered solutions, and have found that this method is by far the most reliable for purposes of comparison and characterisation ; it is of even greater value in this connection than a study of the absorption spectrum, for by its means various properties, such as *pseudo*-base formation and colour base precipitation, ease of oxidation, etc., are incidentally revealed, whereas different anthocyanidins, such as peonidin and malvidin, may exhibit identical absorption spectra. The buffer solutions used consisted of phenylacetic acid, boric acid and potassium dihydrogen phosphate (0·02 grm. mol. each), together with n c.c. of 0·2 N sodium hydroxide, dissolved in water and made up to 1000 c.c. The approximate P_H of each solution, found by indicators, is given, and the results obtained with apigenidin chloride, pelargonidin chloride, cyanidin chlorides, 5-*o*-benzoylcyanidin chloride, peonidin chloride, malvidin chloride, cyanin chloride and malvin chloride. Results with other anthocyanins will be recorded later. It is hoped that the data will be found useful for the identification of anthocyanidins derived from natural sources. Chrysanthemin chloride has been proved to be the 3-glucoside of cyanidin chloride. Contrary to the results of Nierenstein, the authors emphatically affirm that pure synthetic 3:5:7:3′:4′-pentahydroxyflavylium chloride, best prepared by hydrolysis of its benzoyl derivative, exhibits no divergencies from cyanidin chloride, and that the constitution of cyanidin chloride in its main structural outlines is firmly established. P. H. P.

Occurrence of Sucrase in Must and Wine. C. von der Heide and H. Mändlen. (*Z. Unters. Lebensm.*, 1929, **57**, 13–36.)—The presence of sucrase in wine may be demonstrated by the gradual decrease in specific rotation of sucrose. Sucrase was detected in wines, grapes and musts. Its effect is particularly marked with new wines and wines containing yeast deposits, but in the course of time it becomes gradually inactive, probably on account of the combined influence of acid and alcohol. The actual life of the sucrase depends on the sugar, alcohol and acid concentrations, and on the temperature of storage, but is not usually more than 5 years. The enzyme is derived from the yeast or the grapes, and is partly or completely destroyed by heat. The conclusions of previous workers are critically discussed in the light of these results. J. G.

Specific Colour Reaction for Ergosterol. O. Rosenheim. (*Biochem. J.*, 1929, **23**, 47–53.)—The unique function of ergosterol as the parent substance of vitamin *D* made it desirable to find a colour reaction for it, by means of which it could be detected in the presence of other sterols. The property of formaldehyde of moving the colour from the red into the blue part of the spectrum in the usual colour reactions of sterol suggested a method. It was found that ergosterol gives a characteristic blue colour reaction with chloral hydrate, and also with trichloroacetic acid, whilst all the other naturally occurring sterols investigated, when purified from ergosterol, remain colourless under the same conditions. A few crystals of ergosterol, added to about 0·5 grm. of chloral hydrate, liquefied by warming on a water-bath, dissolve, and immediately give rise to a carmine red solution (absorption band 500$\mu\mu$), which changes within a minute into a green,

and finally into a deep blue, which persists for a considerable time. Esters of ergosterol react in the same way. The colour is discharged rapidly by water or alcohol, but a saturated aqueous solution of chloral hydrate (80 per cent.) reacts typically when a drop of concentrated hydrochloric acid is added. Ergosterol dissolved in freshly distilled anhydrous chloral gives the same colours on the addition of one drop of water. An aqueous solution of trichloroacetic acid (9:1), added to ergosterol dissolved in a few drops of chloroform gives an immediate red solution (band at 500$\mu\mu$), which gradually changes into a clear blue (bands at 570–580 and 650–680$\mu\mu$), without showing the intermediate green phase. This occurs at room temperature, and the final blue solution may be diluted with the reagent or with chloroform. The sensitiveness of the reaction is of about the same order as that of the usual sterol reactions, *i.e.* 0·005 mgrm. may be determined. In contradistinction to naturally occurring sterols, it was found, when studying the reaction of sterol derivatives, that the production of an immediate red colour (band at 500$\mu\mu$) with either of the reagents, is specific for the $\Delta^{1,2}$ (or $\Delta^{1,13}$) linkage of the sterol ring system. It is suggested that the primary reaction in all sterol colour reactions consists in the shifting of the double linkage into the $C_{1,2}$ (or $C_{1,13}$) position, and the subsequent formation of coloured carbonium salts. Thus the primary red phase of the ergosterol reaction appears to be due to the presence of the $\Delta^{1,2}$ linkage. Heilbron, Morton and Sexton (*J. Chem. Soc.*, 1928, 47) inferred "that of the three double bonds in ergosterol, two occupy the same position as in cholesterilene." Since cholesterilene gives the red reaction but not the blue, the final blue stage of the ergosterol reaction may justifiably be ascribed to the influence of the third double linkage, the position of which is at present unknown.

P. H. P.

Vitamin Content of Honey. E. Hoyle. (*Biochem. J.*, 1929, **23**, 54–60.)—The experiments recorded in the literature suggest that honey is not a good source of vitamins. However, since these tests were made, vitamin research has progressed considerably, and it therefore seemed advisable to test honey by the more refined methods now available. Two representative samples, one a fresh English comb honey and the other a West Indian granular honey, were obtained for the purpose, and tested, and both were found to be deficient in vitamins *A*, B_1, B_2, *C* and *D*. Tables and curves show the results. Therefore, as shown by other workers, honey is not a source for these vitamins, and this deficiency is not due to deterioration consequent on treatment or storage. P. H. P.

Vitamin *D* and Resistance of Chickens to Parasitism. J. E. Eckert and L. A. Spindler. (*Amer. J. Hyg.*, 1929, **9**, 292.)—The four experiments given were designed to show whether the power of resistance of chickens to nematode worms (*Ascaridia lineata*, Schneider) was decreased by the absence of vitamin *D* in their diet. The criteria, whether the resistance to parasites was lowered, were the number and length of the worms in the intestines of the chickens at the end of the experiments (3 weeks after being infected with parasites). In the first experiment, the 10 chickens fed on vitamin *D*-deficient diet, failed to develop

rickets (judged by absence of leg weakness) apparently because of the inclusion of potassium phosphate in the salt mixture used in the diet. Resistance was not lowered. In the second experiment (potassium phosphate excluded) leg weakness developed in the minus *D* group on the 12th day. The minus *D* group and the plus *D* group were infected with parasites four days later. Resistance was again not lowered. In the third experiment neither group was infected till the birds were 72 days old, thus allowing more power of resistance to develop in the plus *D* group. In this experiment, in which cod-liver oil was the source of the vitamin, the average number and size of the worms in the minus *D* group showed a lowering of resistance, but this might be attributed to the presence of vitamin *A* in the cod-liver oil. In the fourth experiment vitamin *D* was supplied by daily exposure to a mercury vapour lamp. Judged by the number and size of the worms, resistance was not lowered, though, judged by the rate of growth, the effects of the parasites were more severe in the minus *D* group, indicating that vitamin *D* is a factor in protecting chickens against the effects of this nematode. R. F. I.

Bacteriological.

Bactericidal Action of the Nitroso-Compounds. E. A. Cooper and R. B. Haines. (*Biochem. J.*, 1929, **23**, 10–16.)—The nitrosoanilines are more effective germicides than the corresponding nitrosophenols. Nitrosoaniline will inhibit bacteria in concentrations of 1 in 100,000, but nitrosophenol is inhibitory in concentrations of not lower than 1 in 20,000. Both types of compounds show their high germicidal power only in long period bactericidal tests. A study has now been made of (1) the possible application of the nitrosoanilines as internal disinfectants, and (2) the mechanism of their bactericidal activity. The results show that an essential condition for the bactericidal action of the nitrosoanilines is the maintenance of the aminonitrogen in the tervalent state. The hydrochloride and methiodide are weak germicides. Nitrosoaniline and nitrosodimethylaniline are slightly soluble in water. The inhibitory concentration of nitrosodimethyl-aniline (*B. coli*, 48 hours at 37° C.) is 1 in 170,000. However, nitrosodimethyl-aniline is easily soluble in glycerol, propylamine, or formamide without significant loss in germicidal power, and the possibility of its clinical application is at present under investigation. The nitroso-compounds are slowly-acting disinfectants, and exert only a small bactericidal action in short periods, which increases greatly in intensity in periods of 24 to 48 hours. In order to study the mechanism of the action quantitative studies were carried out to ascertain the reactivity of the nitroso-compounds towards amino-acids, proteins, lipins and nucleic acids. They were found to have little or no action on amino-acids and proteins, but to react very gradually with nucleic acid, with the formation of a dark green insoluble product; this compound is possibly a salt of the nitroso-base with the nucleic acid. There is thus a distinct analogy in the case of nitroso-compounds between the process of germicidal action and the reactivity with nucleic acid, an essential constituent of cell nuclear material and associated with the mechanism of growth.

It is therefore concluded that the nitroso-compounds owe their slow germicidal action and marked inhibitory power to their gradual chemical interaction with the nuclear constituents of the cell, thus interfering with and retarding the biochemical mechanism of growth. The influence of concentration on the uptake of *p*-nitroso-dimethylaniline by nucleic acid was studied by dialysis. P. H. P.

Biochemistry of Dry-Rot in Wood. E. C. Barton-Wright and J. G. Boswell. (*Biochem. J.*, 1929, **23**, 110–114.)—The biochemical action of the saprophytic and parasitic fungi which cause decay of lignified tissues is little understood. Mycological literature usually states that the action of the fungal hyphae is to cause delignification of the lignocellulose complex by removal of the lignin, and to leave a residue of cellulose. These results have been mainly attained by the study, on sound and decayed wood, of microchemical tests only, which are of little value in this work. Owing to the conflicting evidence, which is discussed, given by previous workers, an investigation of wood attacked by *Merulius lachrymans* has been carried out with the use of modern methods of cellulose analysis. A study was made of the action of the fungus on completely decayed spruce-wood (*Picea excelsa*). Through the fungus the wood loses weight, and is converted into the so-called touch-wood, which powders easily, to give a brown dust. A comparison table of the analyses of the sound and decayed spruce-wood is given. Direct determinations of the cellulose and lignin in the decayed wood show decrease of the former and increase of the latter, and determination of the methoxyl groupings confirm the increase of the lignin. There is shown an increase of 57 per cent. of lignin, and a decrease of 60 per cent. of cellulose. Therefore there is no delignification of the wood by the fungus ; the main attack is confined to the cellulose. The hexosans, mannan and galactan, are also removed, and it is suggested that *M. lachrymans* first attacks these two easily hydrolysed bodies, and then the cellulose. The fungus is very sensitive to the presence of acids ; coniferous (soft) wood can be made resistant to *Merulius* by impregnation with tannic acid. The presence of acids produced by hydrolysis would hamper the fungus in its attack on the wood, and it may be on this account that the hemicelluloses are not affected. Therefore the effect of the fungus *Merulius lachrymans* (the cause of dry rot in wood) is to remove the galactan, mannan and cellulose fractions, whilst the hemicelluloses and lignin are not affected, *i.e.* no delignification of the woody tissues takes place. P. H. P.

Toxicological and Forensic.

Pharmacology and Toxicology of Tetrachlorethylene. P. D. Lamson, B. H. Robbins and C. B. Ward. (*Amer. J. Hyg.*, 1929, **9**, 430.)—The absorption of tetrachlorethylene by the blood, lung and liver, its pathological effect, and its toxicity have been contrasted with those of chloroform and carbon tetrachloride. If normal dogs are given doses of tetrachlorethylene up to 10 c.c. per kilo. (50 times the therapeutic dose) no indication of absorption is to be observed. If larger doses are given, or if doses of 4 c.c. or more per kilo. are given in

cases where the intestine contains fat, absorption will be observed in all cases, though the degree of absorption varies greatly with the species of animal. Alcohol or low calcium balance greatly increases the toxicity of carbon tetrachloride, but out of 18 dogs treated with doses of from 4 to 15 c.c. of tetrachlorethylene per kilo., with 4 c.c. of alcohol per kilo., 15 recovered with no apparent functional or pathological disturbances. Dogs can be completely anaesthetised if they inhale tetrachlorethylene in concentrations of 62 mgrms. per litre. Since tetrachlorethylene has a much higher boiling point than carbon tetrachloride or chloroform, it was found impossible to cause surgical relaxation even after warming it, but with the cone method any degree of anaesthesia could be induced. If tetrachlorethylene is inhaled or injected intravenously in amounts, death may take place at once. Dogs given doses up to 4 c.c. per kilo. at intervals of 2 or 3 days for several months show no pathological changes in the liver; this contrasts very favourably with the widespread destruction of liver tissue brought about by carbon tetrachloride. Chloroform causes functional disturbance of both liver and kidney. The precautions necessary in giving carbon tetrachloride are unnecessary in giving tetrachlorethylene, although it is suggested that they be observed until this new drug has been more extensively used on man. The experiments indicate that tetrachlorethylene could be used in the treatment of hookworm disease with far greater safety than either oil of chenopodium or carbon tetrachloride. R. F. I.

Cellular Toxicity of Gaseous and Volatile Poisons. (Mme.) S. Lallemand. (*J. Pharm. Chim.*, 1929, **9**, 380–390.)—Exposure of freshly-laid eggs to the action of different gases and vapours in a closed vessel for various periods shows that the eggs develop normally on subsequent incubation after remaining for 8 days in hydrogen, nitrogen, oxygen, or carbon monoxide, which are, therefore, fundamentally non-toxic. Nitrous oxide is slightly toxic, and coal gas more so (toxic time 6 days); then follow carbon dioxide (3 days), acetylene (2 days), chlorine (5 hours), sulphur dioxide and hydrogen chloride (2 hours), ammonia and hydrogen sulphide (3 minutes). The saturated vapours (at 18° C.) of nitric acid, naphthalene, turpentine oil, petrol, aniline, and camphor are not toxic, and those of nitrobenzene and phenol only slightly toxic. For other vapours the toxic times are: iodine 8 days; amyl nitrite 5 days; toluene, amyl alcohol, petroleum spirit, chloral hydrate, butyl alcohol, 4 days; carbon tetrachloride, propyl alcohol, bromoform, 2 days; benzene, 18 hours; ether, 10 hours; ethyl alcohol, 9 hours; methyl alcohol, 8 hours; formic acid, 7 hours; acetic acid, acetone, benzyl chloride, ethyl chloride, chloroform, 5 hours; ethyl iodide, 3 hours; ethyl bromide, 2 hours; carbon disulphide, bromine, 1 hour; nitrogen peroxide, 30 minutes. T. H. P.

Effect of Nicotine upon White Mice. C. H. Thienes. (*Amer. J. Hyg.*, 1929, **9**, 500.)—The effect of the common use of tobacco by adolescents upon their growth is unknown, and preliminary experiments on this point by injecting nicotine into growing white mice have been carried out. Although the effects of injected

nicotine may not be quite the same as in actual smoking, yet it is generally agreed that nicotine is one of the chief factors responsible for the effects of tobacco smoking. Thirty-two mice were fed on whole wheat flour, greens, milk, cod-liver oil and raw chopped beef. On the 7th to 10th day after birth fourteen test mice receive injections twice daily, in the loose areolar tissue between the scapulae, of nicotine base in 0·85 per cent. sodium chloride solution. Eighteen controls were injected with salt solution alone. The absolute dose was increased once or twice per week, according to the severity of the symptoms produced by the previous dose. In the first week the average dose was 0·3 micromgrms. per grm. of mouse, and in the eighth week 2·3 micromgrms. Non-fatal doses produced symptoms ranging from mild excitation to severe clonic and tetanic convulsions. The weight curve of the test mice was very close to that of the controls. There was a marked decrease in susceptibility to nicotine as the mice grew larger, considered to be due to the natural resistance of age, rather than to an acquired tolerance. In view of the fact that results different from the above have been reported on rabbits, further experiments on other species are required. R. F. I.

Agricultural.

Determination of Organic Carbon in Soils. G. W. Robinson, W. McLean and R. Williams. (*J. Agric. Sci.*, 1929, **19**, 315–324.)—The carbon is determined by the quantitative oxidation of the organic matter by sulphuric acid in a Kjeldahl apparatus to carbon dioxide, water, and sulphur dioxide, and the determination of the sulphur dioxide produced in the process. The sulphur dioxide is conveniently absorbed in a tower absorber with 0·5 *N* iodine, and, after aeration, the excess iodine is titrated with sodium thiosulphate. Sufficient soil to furnish 0·02 to 0·05 grm. of carbon is used and ground to pass a 100-mesh sieve, and 25 c.c. of sulphuric acid, 5 grm. of potassium sulphate and 0·3–0·4 grm. of copper sulphate are put in the Kjeldahl flask. This method gives results which average 89·6+1·03 per cent. of the combustion figures, so that it is proposed that the percentage of carbon calculated from the sulphur dioxide should be multiplied by the factor 1·116. The method is applicable to carbonate soils without correction for inorganic carbon, and nitrogen can conveniently be determined on the same sample in one series of operations. It is suggested from data with certain peats that the factor 1·724 for converting organic carbon to organic matter is low, and that a fair approximation would be obtained for most purposes by multiplying by 2. D. G. H.

The Pyrogallol Method for the Determination of Nitrates in Soil and Waters. L. U. De Nardo. (*Giorn. Chim. Ind. Appl.*, 1929, **11**, 107–109.)—Nitrates in the small proportions in which they occur in soils or natural waters may be determined by means of their reaction with either pyrogallol or pyrogallol-sulphonic acid. The latter reagent is prepared by dissolving 5 grms. of pyrogallol in 10 c.c. of concentrated sulphuric acid, heating the solution for a few moments

at 80–90° C., allowing the acid formed to crystallise, and dissolving in water to 200 c.c. One hundred grams of the soil, recently sampled, are shaken for 6 hours with 200 c.c. of water, and then filtered through a folded paper. Of the filtrate, 80 c.c. are shaken in a tared flask with 1–3 c.c. of cold saturated aqueous baryta, the liquid being then heated to the boiling point, allowed to stand so that the precipitate settles, and treated with 0·5–1 c.c. of 50 per cent. basic lead acetate solution. After 2 or 3 minutes the excess of lead and barium is precipitated by about 5 c.c. of saturated sodium sulphate solution, the volume being made up to 100 c.c. with water when cold, mixed, and passed through a dry filter. Ten c.c. of the filtrate are transferred to a 50 c.c. flat-bottomed porcelain capsule. If the soil contains more than 0·1 mgrm. of nitrite as N_2O_3 per kilo., this is removed by adding to the 10 c.c. a drop of concentrated urea solution and, with stirring, about 1 c.c. of concentrated sulphuric acid. After 10 minutes the liquid is treated with 0·5 c.c. of the 2·5 per cent. pyrogallolsulphonic acid solution and, slowly and with stirring, with 20 c.c. of concentrated sulphuric acid. After the lapse of an hour the colour developed is compared with the colours obtained under identical conditions with solutions of known nitrate contents.

If this determination indicates more than 0·1 mgrm. of KNO_3 (per 4 grms. of soil), the test should be repeated as follows : Five c.c. of the solution, defecated as above, are treated in the porcelain dish with urea and sulphuric acid, and afterwards with 0·5 c.c. of a solution containing 2·5 grms. of pyrogallol and 0·1 grm. of sodium bisulphite per 100 c.c., and, with stirring, with 25 c.c. of concentrated sulphuric acid. As before, the colour comparison is made after one hour.

If negative results are given by the above tests, the defecated alkaline solution may be concentrated in order that smaller proportions of nitrate may be sought. With suitable modifications the method may be applied to aqueous vegetable extracts, foodstuffs, etc. T. H. P.

Organic Analysis.

Use of Ozone for the Determination of the Constitution of Unsaturated Compounds. J. Doeuvre. (*Bull. Soc. Chim.*, 1929, **45**, 140–152.)—The methylene grouping $CH_2{:}C(CH_3).CH_2$. and the isopropylidene grouping, $CH_3.C(CH_3){:}CH$., in unsaturated compounds of the terpene series, may be determined by subjecting the compounds to the action of ozone, decomposing the resulting products with water, and determining, in the former case, the formaldehyde, formic acid, and carbon dioxide, and in the latter, the acetone formed. In this way the proportions of the two isomerides in a mixture may be ascertained. From 0·01 to 0·02 grm.-mol. of the substance, dissolved in 8 or 10 c.c. of acetic acid mixed with 2 c.c. of recently-boiled distilled water, is placed in the first of four bubbling apparatus, of about 80 c.c. capacity, these being entirely of glass and provided at the ends with cups to make mercury seals. Each of the three other bubblers contains 15–20 c.c. of water to retain the products formed, and in certain cases a fifth, charged with standard baryta solution, is added to absorb carbon dioxide, which is, however,

never formed in appreciable quantity. The bubblers are cooled with ice and an oxygen-ozone mixture is passed through the whole apparatus, the gas stream being stopped 30 minutes after the issuing gas begins to smell strongly of ozone. The contents of all the bubblers, with rinsings, are transferred to a 100 c.c. flask, which is left at the ordinary temperature for 12 hours before analysis.

The formaldehyde is determined colorimetrically with the Grosse–Bohle reagent, prepared by dissolving 1 grm. of rosaniline hydrochloride in 500 c.c. of water, adding a solution of 25 grms. of crystallised sodium sulphite and 15 c.c. of hydrochloric acid (1·12), making up to a litre, and filtering after one or two days. Measured quantities of the hydrolysed solution of the ozonised material are diluted to about 5 c.c. in similar test-tubes, treated with 1·5 c.c. of hydrochloric acid (1·12) and 3 c.c. of the reagent, made up to 10 c.c., and compared after 12 hours with similar tubes containing known proportions of formaldehyde. The results are accurate to within 5 or 10 per cent.

The formic acid is determined by boiling with red mercuric oxide and absorbing the carbon dioxide formed in standard baryta solution. A wide-necked flask of about 80 c.c. capacity is fitted with an air-supply tube reaching almost to the bottom of the flask, and with two absorption apparatus containing about four times the estimated volume of baryta. Sufficient of the solution to give carbon dioxide corresponding with about 10 c.c. of 0·1 *N* baryta is mixed in the flask with slight excess of aqueous sulphur dioxide for 5 minutes, after which about 8 grms. of red mercuric oxide are added, and the flask closed and shaken. When sulphur dioxide is no longer perceptible, the liquid is heated to boiling and kept gently boiling for 10 minutes, the carbon dioxide formed being then expelled by a current of air, free from the dioxide, passing for 15 minutes; a gentle current of air may be passed also during the heating.

To determine the acetone, an aliquot part of the hydrolysed liquid, after removal of the aldehyde and formic acid, is distilled slowly through a column, the condenser tube dipping below the surface of water in a flask cooled in ice-water. The acetone is often accompanied by aldehydic or ketonic substances, which may be destroyed by a second distillation with permanganate in presence of acetic acid, but this treatment also oxidises the acetone to some extent; with 0·01, 0·0057, and 0·0044 grm.-mol. of acetone the losses are 5, 8·8 and 9·6 per cent. respectively. The acetone is finally determined by Messinger's method. When this method is applied to eugenol, secondary transformations occur which vitiate the results. T. H. P.

Microchemical Distinctions of Essential Oils. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, **101**, 191–196.)—In the following microchemical reactions with essential oils the reagents used are as follows:—A. *p*-Nitrophenylhydrazine, 0·5 grm., hydrochloric acid, 1 c.c., glacial acetic acid, 7 c.c., water to make 50 c.c.; B. Phenylhydrazine solution; C. Semicarbazide hydrochloride, 5 grm. potassium acetate, 5 grm., water, 15 c.c.; D. Saturated solution of potassium permanganate in acetone; E. Commercial solution of sodium acid sulphite; F. Thiery's reagent:

a solution of 0·5 grm. of phenolphthalein in 30 c.c. of alcohol mixed with water until turbidity appears, when 20 grms. of sodium hydroxide are added and aluminium powder in small portions. After decolorisation the liquid is made up to 150 c.c. with boiled water.

Bitter almond oil.—A : deep orange red needles ; B : needles and rods ; C : a variety of forms, rods, plates (the latter often with crenated edges), knife-blade and saw-tooth forms, sometimes scissor-like ; D: warmed with a drop of hydrochloric acid, crystals of benzoic acid appear ; E: a great variety of forms, needles prisms, square plates, etc. ; F : red tint.

Anise oil.—A : orange rods ; C : colourless prisms with plates and other forms ; D : the reagent with hydrochloric acid. Rods of anisic acid appear.

Cajuput oil.—A 5 per cent. hydroquinone solution produces, after vigorous stirring, colourless prisms and other forms ; stirring with potassium iodide and iodine solution produces a pasty mass, but if the reagent and oil are cautiously placed in contact, grey, green or violet tree-like forms appear ; potassium bromide-bromine solution produces yellow masses, referable to cineole (eucalyptol).

Clove oil.—Concentrated aqueous and alcoholic alkalis produce precipitates due to eugenol; also, ammonia vapour produces a mass of crystalline crystals, and the oil stirred with a drop of piperazine solution gives a crystalline reddish mass of plates.

Cinnamon oil.—A : orange-red undefined crystalline precipitate. This is a reaction for the aldehyde, as are the following :—C : rods, single or in groups ; F : rods and needles grouped or separate. Solution of benzidine in glacial acetic acid: Yellow precipitate which may grow into groups of needles. With permanganate, crystals of cinnamic acid are formed, and with a concentrated aqueous solution of *m*-phenylene-diamine hydrochloride, orange-crystals at first and then needles ; and with the *p*-hydrochloride dark orange granules, then groups of needles.

Citrus oil.—A : orange granules ; C : slowly small rods, partly in groups.

Eucalyptus oil.—The reactions of cineole as noted under cajuput oil, but stronger.

Fennel oil.—A : abundant orange needles ; C : numerous crystalline and amorphous forms, a right-angled crystal and rods in saltire and groups. Oxidation gives results similar to those with anise oil.

Cherry laurel.—Similar reactions to bitter almond oil.

Oil of pulegone.—A: numerous fine dendritic orange-red forms, probably derived from pulegone.

Oil of sassafras.—Oxidised with D. and sublimed on an asbestos plate after removal of the acetone, the sublimate will contain piperonal (from safrole). The odour, as well as the orange-red needles with reagent A, are distinctive.

Mustard oil.—Colourless rods and prisms with 50 per cent. piperazine solution ; with bromine water or potassium bromide and bromine solution, amorphous yellow precipitate ; ammonium silver nitrate gives silver sulphide.

Oil of thyme.—A drop mixed with sodium hydroxide solution, then with a concentrated potassium iodide and iodine solution produces in the cold, or on slightly warming, a red precipitate of dithymol di-iodide. If a drop of thyme oil is added to a mixture of zinc chloride and phthalic anhydride, and the mixture melted in a small test tube, a red mass will be formed. On cooling, if water is added and then excess of sodium hydroxide solution, a blue liquid is produced. (phthalein reaction.) The result is due to thymol. Illustrations of many of the crystals are given. D. G. H.

Identification of Rayon (Artificial Silk). W. D. Grier. (*Ind. Eng. Chem.*, 1929, **21**, 168–172.)—Microscopical examination of the fibres, and particularly of their cross-section, affords a reliable means of distinguishing between the four general types of artificial silk now on the market, namely, viscose, cuprammonium, nitro, and acetate silks. The first three also polarise brilliantly, acetate silk only feebly. As regards chemical tests, nitro silk gives a very distinct reaction with diphenylamine and sulphuric acid reagent, and viscose may be detected by a test proposed by Schreiber and Hamm, which depends on the formation of minute residual amounts of sulphur compounds when the material is heated on a steam-bath with very dilute sulphuric acid. Acetate silk dissolves readily in acetone. W. P. S.

English Bookbinding Leathers. R. W. Frey, L. R. Leinbach and E. O. Reed. (*J. Amer. Leather Chem. Assoc.*, 1929, **24**, 190.)—Twenty-three whole skins tanned and dressed by English tanners for book-binding purposes have been examined physically and chemically. The physical measurements include those of stretch, tensile strength and weight per unit area. The chemical determinations include the percentages of mineral acid, grease and water-soluble matter, also the degree of tannage (parts of fixed tan per 100 parts of hide substance), and whether the tan was of the pyrogallol or the catechol type. The tensile strength varied in 13 goat skins from under 2000 to over 3000 lbs. per sq. in.; in 6 calf skins from under 2000 to over 3500 lbs. All the leathers labelled as being free from mineral acids contained less than 0·3 per cent. of acid (as sulphuric acid), as determined by the Procter-Searle method. In those not guaranteed, the acid as sulphuric acid varied from 0 to 2·2 per cent., the latter giving a water extract of P_H value 2·4. Five of the leathers had a figure, for the degree of tannage, of 70 or more, seven 60 to 70, three 55 to 60, and seven less than 55. It is stated that too high a figure results in a tax on the life of the fibre when the leather is submitted to repeated bending. Fifteen of the leathers, mostly goat skins, contained under 3 per cent. of matter soluble in petroleum spirit, the highest figure being 11·1. Too low a grease content is said to be one of the causes of deterioration of leather bookbindings.

(*Abstractor's Note.*—No conclusions as to the relation of these data to the life of the leathers can be drawn until books bound with these leathers have been submitted to conditions of atmosphere and light for 15 to 20 years.) R. F. I.

Quantitative Analysis of Tin in Organic Compounds. H. Gilman and W. B. King. (*J. Amer. Chem. Soc.*, 1929, **51**, 1213–1215.)—A slight excess of an approximately 4 per cent. solution of bromine in carbon tetrachloride is added to 0·5 grm. of sample in a cooled, tared 60 c.c. porcelain crucible, and is followed by 2 c.c. of a mixture of concentrated nitric and sulphuric acids (1:6). After the violent reaction has ceased, 4 c.c. of a 1:1 mixture of the acids are added, then 2 c.c. of nitric acid, and finally 5 c.c. of fuming nitric acid. After 30 minutes on the steam bath the oxides of nitrogen, the carbon tetrachloride, and finally the sulphuric acid, are removed at a low heat, and the greyish residue ignited till constant in weight and weighed as stannic oxide. The maximum recorded error for a number of organo-tin compounds is about 0·5 per cent. J. G.

Inorganic Analysis.

Determination of Hydrogen Ion Concentration by a Modified Colorimetric Method. D. H. Cameron. (*J. Amer. Leather Chem. Assoc.*, 1929, **24**, 76.)—This method was devised to overcome inaccuracies arising from the fact that the standard colour tubes are not permanent, that the indicator solutions are not stable, and that varying shades of colour may develop in a series of tubes using the same indicator at the same P_H. The procedure eliminates the need of prepared colour standards. The approximate P_H of the unknown solution is first determined. Two 50 c.c. Nessler cylinders of uniform diameter are taken. Into one are put 25 c.c. of the unknown solution with a volume of diluted indicator measured by a small pipette. Into the other cylinder are introduced 25 c.c. of the necessary buffer solution (one of the three given below) with the same volume of the same diluted indicator; 0·2 *N* sodium hydroxide (free from carbonate) is added till the colours in both cylinders are the same after an equal volume of water has been added to the unknown solution. The volume of sodium hydroxide required is noted, and from a curve or table based on Clark's figures the P_H value can be deduced. The three standard buffer solutions given are 0·1*M* potassium hydrogen phthalate for the range 4·0 to 5·8, 0·1 *M* potassium dihydrogen phosphate for the range 5·8 to 7·8, and 0·1*M* boric acid for the range 7·8 to 10·0.

P_H values below 4·0 may be obtained by using potassium hydrogen phthalate and adding 0·2 *N* hydrochloric acid. The method works well where there is no scarcity of sample and where the test solution is colourless. Tables for the range 4·0 to 10·0 are given. R. F. I.

Potentiometric Titration of Ammonia. E. B. R. Prideaux. (*J. Soc. Chem. Ind.*, 1929, **48**, 87–88T.)—Although ammonia cannot be titrated with the hydrogen electrode, it may be back-titrated if the cell-combination Pt, | quinone, quinhydrone, HCl, NH_4Cl | saturated KCl | saturated calomel electrode, is used. Ammoniacal gas liquor (20 c.c. of an approximately 0·1 *N* solution) was pipetted into an excess of 0·1 *N* hydrochloric acid, boiled for an hour to remove volatile acids, cooled, the quinone-quinhydrone added, and the excess of acid determined

potentiometrically with 0·1 *N* alkali. The potentials (*E*) of the theoretical end-points may be determined for different concentrations (*c*) of ammonium chloride from the equations $E=0{\cdot}453-0{\cdot}058 \log [H^{\cdot}]$ and $P_H=4{\cdot}685-0{\cdot}5 \log c$, *E* being 141, 137 and 132 millivolts when *c* is 0·04, 0·03 and 0·02, respectively. The accuracy of the titration is that obtainable with the weight burette. The method is therefore preferable to titration with methyl red indicator, especially since it may be used with coloured or turbid solutions, and provides a warning of the approach of the end-point. J. G.

Determination of Tin by Rapid Electrolysis. J. Švéda and R. Uzel. (*Collection des Trav. Chim. Czechoslovaq.*, 1929, **1**, 203–222.)—Stannous or stannic tin (0·5 to 0·05 grm.) may be deposited from 200 c.c. of solution in the presence of 10 grms. of ammonium oxalate, 5 grms. of oxalic acid and 2 grms. of hydroxylamine hydrochloride (or 4·724 grms. of sulphate) by electrolysis for 25 minutes at 60 to 70° C. with a current density of 5 amps. at a voltage of 2·5 to 3·5 volts. The solution, which has been well stirred, is maintained at 65° C. by the current, and is finally washed out with a large volume of water without interrupting the current. The deposit is bright and adherent, and an accuracy of $\pm 0{\cdot}32$ per cent. is obtainable for from 0·1 to 0·5 grm. of tin. Deposits of stannous tin from neutral solutions were powdery, whilst the deposition of stannic tin from alkaline solutions was too slow. The electrodes were of platinum-iridium wire gauze, the cathode being copper-plated. For deposition of tin from ammonium thiostannate solutions the copper-plated cathode was also tin-plated. In this case electrolysis was slow, but gave satisfactory, though slightly high, results in the presence of 30 c.c. of a 40 per cent. solution of sodium sulphite as depolariser for polysulphide ions. The hydroxyl ion concentration was maintained below a certain limit by the addition of 3 to 6 grms. of an ammonium salt of a strong acid. Satisfactory results were also obtained with 200 c.c. of electrolyte containing 10 c.c. of hydrochloric acid and 2 grms. of hydroxylamine hydrochloride. With more than 0·5 grm. of tin the deposit is improved by the addition of 0·4 grm. of ammonium persulphate, in addition to the hydroxylamine salt. Hydrazine salts produce coarse, crystalline deposits. J. G.

Confirmatory Test for Aluminium. R. Gemmill, R. Brackett and C. R. McCrosky. (*J. Amer. Chem. Soc.*, 1929, **51**, 1165.)—A piece of pure asbestos fibre, half the size of a pea, is impregnated with 0·05 *N* cobalt nitrate solution and ignited on a platinum wire. It is then dipped in a solution of the aluminium hydroxide precipitate in the minimum amount of nitric acid and re-ignited. The test (formation of a blue residue) is sensitive to 0·2 mgrm. of aluminium or 0·5 mgrm. of zinc, and is unaffected by sodium (*cf.* Pañganiban and Soliven, ANALYST, 1928, **53**, 616). J. G.

Analytical Chemistry of Beryllium. Part II. L. Moser and F. List. (*Monatsh. Chem.*, 1929, **51**, 1133–1141.)—Beryllium cannot be separated from the alkaline earths by ammonia, even that free from carbonate; on the other hand,

hydrolytic precipitation with ammonium nitrite and methyl alcohol (Part I, ANALYST, 1928, **53**, 402) provides an efficient separation from *strontium*, *calcium* and *magnesium*. *Barium* is best separated as sulphate, the precipitation being effected gradually; the beryllium in the filtrate is precipitated by tannin. The nitrite method can also be used successfully for the separation from *zinc*, *cadmium*, *nickel*, *cobalt*, *manganese*, and *thallium*. Zinc and cadmium may also be precipitated by hydrogen sulphide, manganese by ammonium persulphate, from feebly acid sulphate solution. Thallium is precipitated as chromate in the concentrated filtrate from the beryllium precipitation (ANALYST, 1928, 459), and, if the solution to be hydrolysed with ammonium nitrite is acid, it must be neutralised with sodium carbonate, not ammonia, as thallous chromate is slightly soluble in presence of ammonium chloride.

Arsenic and *antimony* may be separated from beryllium by hydrogen sulphide precipitation in hydrochloric acid of such concentration as to yield precipitates free from adsorbed beryllium: the black, crystalline modification of antimony trisulphide can be obtained by known means. The separation of *tin* by hydrogen sulphide fails by reason of beryllium adsorption in the stannic sulphide. The following method is given: the strongly acid, boiling chloride solution is treated with 5 c.c. of 10 per cent. tannin solution, and 10 to 20 grms. each of ammonium acetate and nitrate. The boiling solution becomes turbid, and the precipitate gradually flocculates; flocculation of the tin adsorption complex is complete after one hour's heating on the water-bath. The precipitate is collected and washed with hot ammonium acetate solution containing a little tannin. If more than 0·2 grm. of tin is present, the precipitate is dissolved in hot, strong hydrochloric acid, and the operation repeated. After being dried, the precipitate is ignited gradually, finally on a blast burner, and weighed as SnO_2. The combined filtrates are evaporated, neutralised with ammonia, and the beryllium precipitated with tannin.

For the systematic separation of beryllium from a solution containing other metals, the acid solution is first precipitated with hydrogen sulphide; the filtrate is oxidised with bromine, the excess of which is boiled off. Barium, if present, is removed next as sulphate; the tervalent and quadrivalent metals, together with the beryllium, are then precipitated by nitrite hydrolysis. The precipitate is dissolved in nitric acid, and all the metals present, with the exception of beryllium, precipitated by tannin from acetate solution: the filtrate is made ammoniacal and treated with more tannin, whereby the beryllia is isolated. W. R. S.

Analytical Chemistry of Gallium. (Part II.) L. Moser and A. Brukl. (*Monatsh. Chem.*, 1929, **51**, 73–81.) (Part I, ANALYST, 1929, 64.)—So far, no satisfactory methods for the quantitative separation of gallium from metals of the ammonia group are known. The authors show that a number of satisfactory separations can be effected by means of cupferron. *From aluminium*, *chromium*, *indium*, *uranium*, *cerium*: the chloride or sulphate solution (0·01 to 0·3 grm. Ga), which may contain ammonium salts, is adjusted with 2 *N* sulphuric acid to a

bulk of 200 to 300 c.c., and treated in the cold with 0·1 grm. of cupferron in 6 per cent. solution; a white flocculent precipitate is obtained, which clots together above 30° C., and can then be crushed with a glass rod to a crystalline mass; it is collected on paper with the help of gentle suction. The first filtrate, which is always cloudy, is re-treated with 1 to 2 c.c. of reagent, and again passed through the same filter. If now it remains clear after an hour's standing, the precipitation may be considered complete; if not, the re-treatment must be repeated. The precipitate is washed with 2 *N* sulphuric acid; it must be strictly free from chlorides as gallia can be volatilised completely by heating with ammonium chloride. The precipitate is gently, then strongly, ignited in a porcelain crucible, and weighed as Ga_2O_3, which is hygroscopic. Double precipitation is necessary if the quantity of aluminium present exceeds 2 grms. In the separation from indium, the washing of the precipitate must be very thorough, and cupferron should be added to the acid wash-liquor. If indium predominates, the precipitation is repeated; a small quantity of india is detected by the yellow tint of the gallia during ignition. In the separation from uranium, care must be taken to prevent any reduction, as quadrivalent uranium is quantitatively precipitated by cupferron. *From iron.*—(*a*) For little gallium from much iron, the acid solution free from ammonium salts is almost neutralised with sodium carbonate, decolorised in the cold with an excess of sodium thiosulphate, and boiled for 15 minutes, 10 c.c. portions of aniline being added at 5-minute intervals, to depress the final acidity, and thereby complete the precipitation of the gallium hydroxide. The hot solution is filtered, the precipitate carefully washed with hot water, and ignited. It always contains a little iron, and is treated according to (*b*) after fusion with bisulphate. (*b*) Little gallium from little iron: the solution is treated with a moderate excess of 10 per cent. sulphosalicylic acid solution and enough ammonia to produce a clear, pale red solution, which is boiled and treated with hydrogen sulphide till cold. The ferrous sulphide is filtered off and washed as usual, the filtrate acidified with acetic acid, and boiled free of hydrogen sulphide; gallium is then precipitated by excess of ammonium acetate and tannin, as described in Part I. (*c*) Much gallium from little iron; the nearly neutral solution is slowly poured into hot ammonia, when ferric hydroxide is precipitated and soluble gallate formed. The iron precipitate containing adsorbed gallia is treated according to (*b*); the gallium solution is acidified with acetic acid and precipitated with tannin (Separation of iron by nitroso-β-naphthol, ANALYST, 1928, **53**, 558.)

W. R. S.

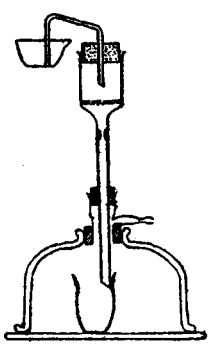
Gravimetric Methods for Vanadium. L. Moser and O. Brandl. (*Monatsh. Chem.*, 1929, **51**, 1121–1132.)—The precipitation of ammonium metavanadate and mercurous vanadate was re-investigated; two new forms of weighing—silver orthovanadate and lead pyrovanadate—are described. *Ammonium metavanadate* was precipitated substantially as in Gooch and Gilbert's process, the alkali metavanadate solution being treated with an equal volume of cold-saturated ammonium chloride solution and a few drops of ammonia, and the liquid evaporated on the water-bath to the original bulk. The precipitate is

collected after 12 hours' standing in the cold, and washed with a minimum of saturated ammonium chloride solution ; it is dried at 110° C., and separated from the filter. This is first heated in a covered platinum crucible to 150° C. for the removal of the ammonium salt, then gradually to a higher temperature with the lid off. When the paper has been burnt off, the added precipitate is heated with the same precautions, as otherwise the ammonium chloride causes volatilisation losses. The molten pentoxide is made to run in a thin layer round the sides of the crucible during ignition at red heat ; any lower oxides are thus re-oxidised. An improved *mercurous vanadate* precipitation method is described ; the boiling alkali vanadate solution, which may contain a little nitric acid but no ammonium salts, is treated with 3 c.c. of 10 per cent. hydrogen peroxide and a large excess of mercurous nitrate solution (the powdered salt treated with hot water) : 0·1 grm. V_2O_5 requires 40, 0·2 grm. 60 c.c. of this solution. For the destruction of the hydrogen peroxide the covered beaker is boiled half an hour ; the precipitate is collected, washed with cold water, dried and separated from the filter, the paper ashed separately, and the precipitate strongly ignited to V_2O_5. If this method is followed, the precipitate consists of sparingly acid-soluble pyro- and orthovanadate, whilst without hydrogen peroxide the more soluble hexavanadate $Hg_4V_6O_{17}$ is obtained. *Silver orthovanadate* is obtained from an alkali vanadate (maximum 0·2 grm.) solution (200 c.c. bulk) treated with 3 grms. of pure sodium acetate, 0·5 c.c. of strong ammonia, and an excess of silver nitrate. The liquid is boiled and transferred to the water-bath ; after half-an-hour it is tested with a little more silver nitrate, and in case of a turbidity the liquid is boiled till clear. The dense, brown precipitate, Ag_3VO_4, settles well ; it is collected in a porous porcelain crucible, washed with hot water, dried at 110° C., and ignited gently with the crucible placed inside a larger one. If the vanadate solution is alkaline it is boiled and treated, drop by drop, with nitric acid till permanently yellow ; a few drops of ammonia are then added to decolorisation. If acid, the vanadate solution is neutralised with caustic soda. The determination as *lead pyrovanadate* is more tedious than the preceding, though the results are satisfactory. W. R. S.

Reagent for Potassium, Ammonium, Rubidium and Caesium Ions. T. G. Y. Arnal. (*Chim. et Ind.*, 1928, Oct. ; *Ann. Chim. Anal.*, 1929, **11**, 10–11.)—No precipitate results on the addition of 5 per cent. uranyl nitrate solution to a solution of sodium chromate (about 5 per cent. CrO_4), or to a solution of similar concentration of ammonium chromate, but in the latter case a precipitate forms on warming, and with a similar potassium chromate solution a precipitate forms in the cold. The precipitates are soluble in concentrated solutions of sodium chloride and more soluble in solutions of uranyl nitrate and in acids, and are but little soluble in alcohol. Thus if a uranyl nitrate solution is added to one of sodium chromate, so that there is a stoichiometric formation of uranyl chromate, a yellow precipitate will be formed on addition of potassium. Similarly, rubidium and caesium ions may be detected. D. G. H.

Influence of Lithium, Rubidium, Caesium, and Magnesium upon the Detection of Potassium by Zirconium Sulphate. R. D. Reed and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1929, **51**, 1062–1065.)—The authors' reagent (ANALYST, 1928, **53**, 456) will detect 1·0 mgrm. or more of potassium in 2 c.c. of reaction mixture in the presence of 50 mgrms. of lithium, 16·6 mgrms. of rubidium or of 11·6 mgrms. of caesium sulphate. It will detect 0·5 mgrm. or more in the presence of 50 mgrms. of magnesium sulphate, but not if 11·6 mgrms. of caesium sulphate are present. In such cases a blank test should always be carried out. Comparison with other reagents (sodium cobaltinitrite, chloroplatinic acid, and perchloric acid) showed that zirconium sulphate alone is a selective reagent for potassium in the presence of the fifth-group elements. J. G.

Separation of Lithium from Potassium, Sodium and Magnesium. L. Moser and K. Schutt. (*Monatsh. Chem.*, 1929, **51**, 975–994.)—The accuracy of the published methods was tested, with results given below. *Separation from sodium and potassium.*—The only serviceable methods are those based on the solubility of lithium salts in certain organic solvents; the chlorides of sodium and potassium are too soluble in strong hydrochloric acid for a quantitative separation. Extraction of the mixed chlorides with pyridine, commercial or anhydrous, gives low values for lithium, which can always be detected in the insoluble residue. The method of Winkler (extraction of the chlorides with absolute isobutyl alcohol) was followed with very slight modifications, and proved to give excellent results. Greater care was taken to ensure the complete dehydration of the alcohol, *i.e.* by three hours' boiling under a reflux condenser with barium oxide and distillation. The two principal changes effected were: (1) The substitution of a sintered glass crucible for a filter paper, as it was ascertained that the paper adsorbs appreciable amounts of lithium salt; (2) syphoning of the lithium extract on to the porous glass crucible instead of pouring the liquid out of the basin. This mode of working obviates the losses due to creeping of the solvent over the edge of the containing vessel. The syphon is worked by suction, its descending member passing through a stopper at the top of a filtration crucible of special construction (see diagram). A deduction of 0·0005 grm. is made from the weight of Li_2SO_4 found: this amount is added to the weight of $K_2SO_4+Na_2SO_4$. Smith and Ross's method (ANALYST, 1925, 307)—separation of sodium and lithium perchlorates from the potassium salt by a 1:1 mixture of ethyl acetate and *n*-butyl alcohol and subsequent action of a 20 per cent. solution of hydrogen chloride in *n*-butyl alcohol on the soluble perchlorates, sodium chloride being precipitated—was found to give low lithium results; all the sodium fractions gave strong lithium lines. *Separation from magnesium.*—Conversion of magnesium chloride into the oxide by double evaporation of the solution with yellow mercuric oxide (Berzelius) does not give chlorine-free magnesium oxide. The precipitation of



magnesium chloride solutions with alcoholic ammonium carbonate, though quantitative, gave high magnesium results, due to the adsorption of lithia by the magnesium ammonium carbonate, even after double precipitation. The only process of separation that gives correct results is Berg's *o*-hydroxyquinoline method (ANALYST, 1927, **52**, 431). The solution of the chlorides, containing ammonium chloride (80 to 150 c.c. bulk), is precipitated at 70° C. with a 2 to 5 per cent. alcoholic solution of the reagent till the solution is yellow, the liquid being meanwhile heated to boiling. After cooling, the precipitate is collected on a porous glass crucible, well washed with hot water containing a little ammonia, and dried at 105° C. The filtrate is evaporated in a platinum basin, the residue dissolved in a little dilute hydrochloric acid, and the solution filtered into a tared platinum crucible; the lithium is determined in the usual manner as sulphate. If potassium and sodium are also present, the filtrate from the magnesium precipitate is evaporated to dryness, the residue gently heated for the removal of the ammonium salts, and the lithium in the fixed residue separated from potassium and sodium by isobutyl alcohol. W. R. S.

Ceric Sulphate in Volumetric Analysis. V. Potentiometric Study of the Reaction between Ferrocyanide and Ceric Ions. N. H. Furman and O. M. Evans. (*J. Amer. Chem. Soc.*, 1929, **51**, 1128–1133.)—The reaction $Ce^{\cdots\cdot} + Fe(CN)_6'''' \rightleftarrows Ce^{\cdots} + Fe(CN)_6'''$ proceeds quantitatively from left to right in acid, and from right to left in alkaline solution, and the end-point may be accurately determined by Furman's potentiometric method (ANALYST, 1928, **53**, 302). A stable 4*N* ceric sulphate solution was prepared by dissolving commercial rare earth oxides containing 45 per cent. of CeO_2 in sulphuric acid, and was standardised potentiometrically against pure sodium oxalate in the presence of hydrochloric acid (*cf.* Willard and Young, *id.*, 404). The potassium ferrocyanide solution, which should be about 0·1 *N*, is titrated with the ceric sulphate solution at 25° C. in the presence of sulphuric acid not exceeding 5 *N* or hydrochloric acid 0·2 to 2 *N* in strength. If the acidity is too low a white precipitate is formed, and if too high the end-point is sluggish. At the end-point there is a potential jump of at least 0·2 volt per 0·05 c.c. of 0·1 *N* ceric solution, while the sharp disappearance of the green colour, due to ferric ferrocyanide produced from traces of ferric iron, when the last traces of ferrocyanide are oxidised, may be used as a visual end-point. The reverse titration is accurate only if the major portion of the reagent is added rapidly, and it is not recommended for general use. J. G.

Micro-Titration of Iodides, in Absence or in Presence of Large Proportions of Nitrite. J. F. Reith. (*Rec. Trav. Chim. Pays-Bas*, 1929, **48**, 386–390.)—Quantities of iodide ion as small as (0·5γ = 0·005 mgrm.) may be determined by the bromine and sulphuric acid method, which is carried out as follows: The iodide solution (not more than 1 c.c.) is pipetted into a 25 c.c. Erlenmeyer flask and is rendered acid by dropwise addition of 0·5 *N* sulphuric acid, the reaction being tested by streaking methyl-orange paper with a platinum wire; an excess of two

drops of the acid is added, the P_H value being then about 1·6. Three drops of saturated bromine water, sufficient water to give a total volume of 2 c.c., and a little powdered pumice (0·5–0·8 mm. size) are added, and the flask placed obliquely on a very hot sand-bath. The liquid is boiled for 45 seconds after a distinct stream of steam begins to issue and is then cooled. The subsequent titration is made in artificial light, such as that from a Phillips sunlight lamp, direct radiation from which is avoided. The liquid is treated with 0·1 c.c. of 5 per cent. potassium iodide solution and 3 drops of 0·5 per cent. starch solution, and titrated slowly with 0·001 *N* thiosulphate solution, which is allowed to flow out near the bottom of the flask, held obliquely, from a graduated pipette holding 0·1 or 0·3 c.c. and reading to 0·001 c.c. Towards the end-point, 0·002 c.c. quantities of the solution are run in, comparison of the colour before and after mixing the liquid being made. One c.c. of 0·001 *N* thiosulphate corresponds with 21·15γ of iodide-ion, and the correction for the sensitiveness of the starch-iodine reaction is $v \times 0{\cdot}1$ mgrm. of iodine at 15–18° C., v being the volume of the liquid after completion of the titration. For quantities between 0·5 and 1·5γ of iodide-ion, this method gives results accurate to less than 5 per cent., and for 1·5–10γ, less than 2 per cent.

If nitrite is present, its disturbing influence may be avoided by the following azide method. The solution (at most 1 c.c.) is treated in the Erlenmeyer flask with excess of 5 per cent. sodium azide solution (1 mgrm. of HNO_2 requires 1·7 mgrm. NaN_3), and acidified with 2 *N* sulphuric acid, vigorous evolution of nitrogen and nitrous oxide occurring. If the odour of azoimide is not detectable, more azide solution must be added and the acid reaction of the liquid maintained. Two drops in excess of the acid and three drops of bromine water are added, the further procedure being that of the bromine-sulphuric acid method. T. H. P.

Physical Methods, Apparatus, etc.

Determination of Vapour Densities at Room Temperatures. E. F. Linhorst. (*J. Amer. Chem. Soc.*, 1929, **51**, 1165–1167.)—Two 2-litre round-bottomed flasks connected by an oil manometer (60 cm. overall length, 5 mm. diameter) may be evacuated simultaneously through a T-piece, the arms of which are provided with stop-cocks and each connected with one of the flasks. The sample is sealed in a Victor Meyer bulb, wired on to the sealed end of the manometer tube projecting inside one of the flasks, the flasks evacuated to a pressure of about 1 cm. of mercury, and the cocks closed. The bulb may then be crushed by turning the arm attached to the T-piece, the end of which projects in the flask and is bent at an angle. If the temperature and increase in pressure are read after a few minutes the molecular weight (M) may be found from the equation $PV = WRT/M$. The minimum vapour pressure of the sample should be at least 4 cm. of mercury at room temperature, or larger flasks or a higher temperature must be used. J. G.

Spectrographic Chemical Analysis. H. Ramage. (*Nature*, 1929, **123**, 601–602.)—The spectrographic analysis of minerals is conveniently carried out with a Hilger (C) quartz spectrograph on 0·5 grm. or less of sample tightly rolled in half an ashless (No. 00) filter paper, which is burnt for 25 minutes in an oxy-hydrogen or oxy-coal gas flame, a quartz lens being used to focus the flame on the slit. If the poles of an arc are placed horizontally in the flame just above the burning roll, the delicacy of the test is greatly increased, and elements such as titanium, molybdenum, tungsten, etc., give lines instead of only a continuous spectrum. Ilford panchromatic plates coated on thin glass are suitable for quantitative work, and the method has been applied to the examination of flue dust for gallium, to the determination of the salt content of different portions of plants grown in different soils or watered with different solutions, and to the determination of rubidium and other elements in blood or milk. Solid vegetable or animal substances may be held in forceps and burnt without the use of filter paper, while for liquids 0·1 c.c. is absorbed on the paper and burnt. J. G.

Barium Sulphate as Indicator of the Efficiency of Sulphuric Acid in Drying Apparatus. G. Boehm. (*Chem. Ztg.*, 1929, **53**, 323.)—Sulphuric acid retains its desiccating properties until it is completely converted into the dihydrate (84·48 per cent. of H_2SO_4), which has the vapour pressure 0·131 mm. at 15° C., whereas that of the trihydrate is 0·651 mm. Addition of about 18 grms. of barium sulphate to each litre of the concentrated acid allows the complete formation of the dihydrate to be detected. Until about one-half of the amount of water required to give the dihydrate has been absorbed, the acid shows no change. With further dilution, the compound $BaSO_4$, $2H_2SO_4$, H_2O is increasingly precipitated in the form of acicular aggregates, which finally render the acid pasty. These crystals are not stable, and when the acid is wholly transformed into the dihydrate, are decomposed into finely crystalline barium sulphate. Thus, the acid need not be replaced so long as it contains acicular crystals. It is advisable to use the purest barium sulphate for this purpose, and the necessary quantity should be dissolved in a small portion of the sulphuric acid at 100° C. and afterwards mixed with the remainder of the acid. T. H. P.

Reviews.

STARCH: ITS CHEMISTRY, TECHNOLOGY AND USES. By LEWIS EYNON, B.Sc., F.I.C., and J. HENRY LANE, B.Sc., F.I.C. Pp. viii+256. Cambridge: W. Heffer & Sons, Ltd. 1928. 12s. 6d.

The authors state in their preface that it is now about forty-five years since a comprehensive text-book on starch has been published in the English language. In view of this fact, it is a curious coincidence that two books on this subject should

be published in the same year. Evidently when the authors' preface was written they were unaware of the book on starch chemistry, edited by Walton (see ANALYST, 1928, **53**, 561), which was published some months earlier than their own. The ground covered is, for the most part, the same in both, but there are considerable differences in treatment, and each has one or two sections which the other has omitted.

In the book under review the authors, after giving a brief history of starch, deal in a very interesting and readable manner with starch in relation to plant metabolism. This is followed by a chapter on the constitution of starch. In this the authors discuss the various attempts which have been made to solve this problem since Kirchoff first discovered in 1811 that starch yields a sugar on hydrolysis with acid. The more recent work of Ling and Nanji, Irvine and others is discussed very clearly and in considerable detail. The following chapter deals with the properties of starch, and this will probably prove the most interesting portion to technical chemists. Much useful information regarding its gelatinising properties, and the viscosities of pastes and solutions of the more commonly used starches are given. In the section on the hydrolysis of starch the action of the various diastatic enzymes is discussed from the more purely biochemical aspect, *i.e.* no reference is made to the technical application of these reactions. The remainder of the chapter deals with its essentially chemical properties.

Chapter V, which is devoted to the microscopy of starch, describes very completely all the well-known starches, and many which are less well known to the British analyst. There are excellent reproductions of 32 photomicrographs of starches, but it is rather unfortunate that the magnification used is not indicated on the plates, and is only referred to in the last paragraph of the chapter. It would appear from the text that the authors intended the plates to follow at the end of the chapter, but the printers have inserted them a few pages in front. No doubt this small defect will be remedied in future editions.

Among the photomicrographs, it is interesting to note, the authors have inserted those of sago and tapioca in the ungelatinised form, as well as in the gelatinised. Generally only the latter are given, but now that the ungelatinised forms are so widely used in the foodstuff industries the former will prove more helpful to the analyst. Some special methods of identifying starches in mixtures are also given.

The next five chapters describe in considerable detail the technical preparation of starch from its various sources; then follows a chapter on the manufacture of such starch products as soluble starch, dextrin, dextrose, maltose, glucose syrups, etc., and numerous references are given to the various patents in connection with their manufacture. It should be noted that the authors confine themselves to starch and its immediate products, and do not deal with cereals or products in the manufacture of which starch or its products are used, beyond briefly outlining in Chapter X some of these industrial applications. In the latter section the authors describe under the term "confectionery purposes," such products as

custard powder, cake mixtures, etc., which, however, are not usually considered confectionery products. On the other hand, the only reference to the use of these substances in the confectionery and jam industries is contained in the previous chapter under the heading of starch sugar. Some reference might have been made to the very pure form of dextrose which the Americans have recently put on the market, and which will probably find use in the manufacture of entirely new types of confectionery, as well as in modifying some of the older forms.

The final chapter deals with the analysis of commercial starch and its immediate products. It does not, however, discuss methods for determining these in articles manufactured from them. A few examples of some of these would have added to the usefulness of the book to the general analyst.

The book, as one would expect from its authors, is very clearly written, and there is a remarkable absence of printers' errors. The printing and illustrations are good, and both Mr. Ward and the printers are to be congratulated on the excellence of the photomicrographs of the starches. It should prove a very useful book of reference to all who are interested in starch and its products.

T. MACARA.

PRACTICAL BACTERIOLOGY. AN INTRODUCTION TO BACTERIOLOGICAL TECHNIC. By FRED W. TANNER, Ph.D., Professor of Bacteriology and Head of the Department, University of Illinois. Pp. xiv+235, with 70 illustrations. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1928. Price 12s. 6d. net.

The Society of American Bacteriologists has made some notable attempts to systematise the science of bacteriology. One activity has been the elaboration by a "Committee on Bacteriological Technic" of "Descriptive Charts." Professor Tanner was a member of the Committee that designed the latest of these charts in 1924. A copy of it is included in the book, and may be taken to exhibit current American opinion as to what morphological, cultural and physiological attributes require to be ascertained in the experimental investigation of an organism. Much of the book is devoted, either avowedly or in effect, to educating students to appreciate and to utilise the scheme for descriptive ends. A feature of this chart is the provision of many strange-sounding, but appropriate, adjectives to characterise the "form," "surface," "elevation," "edge," and "internal structure" of bacterial colonies, also the types of liquefaction in stab cultures, and the forms of growth in streak cultures. The selection of the right adjective, not always an easy decision, is assisted by a glossary and illustrations of colonies.

Another labour of the Society of American Bacteriologists, embodied but not, however, mentioned in the book, proves irksome to some English readers. This is the "Characterisation and Classification of Bacterial Types" which it evolved in 1920, together with its developments. Here the book gives no assistance. Nearly all other authors have recognised that the new classification is still

unfamiliar to many, and give the old as well as the American names. Here we have former nomenclature ignored. While we get accustomed to *Bacillus coli* changing its name to *Bacterium coli*, and then to *Escherichia coli*, while *Bacillus typhosus* goes to *Bacterium typhosum* and on to *Eberthella typhi*, such a name as *Aerobacter aerogenes* is not so easily recognised as identical with *Bacillus lactis aerogenes*, nor is *Serratia marcescens* indicative to many of *Bacillus prodigiosus*. That is, while admitting the American classification, we like to have the old names too.

The book is described as a "laboratory guide for students who are beginning the study of bacteriology," and the underlying idea is "to make students proficient in ordinary technic." It is calculated to do this with suitable students. There is nothing out of place in the book; even a digression on the attempts to explain and those to improve the Gram method of staining are valuable. Though little tangible result seems forthcoming, the recital directs attention to the degree to which chemical attributes, both of bacteria and of the materials used, do profoundly influence the success of the test. It is a striking comment that this dissertation should end with a quotation from C. J. Hucker and H. J. Conn, thus: "After a general survey of nineteen different methods of Gram staining, it is very difficult to select any one method as superior to all the others."

The author places the date of the discovery that some bacteria cells are Gram-positive when young, but Gram-negative when old, as late as 1921. Foulerton, in his classical lecture on Streptothricosis in 1910, gave instances of this obtaining in the Streptotricheae. Since then, but still before 1921, in 1916 the bacillus of malignant oedema, which had previously been characterised as Gram-negative, was found to be so when attenuated, but to be Gram-positive when young. Weinberg's *Bacillus oedematiens*, found in some gas-gangrene wounds during the war, was Gram-positive as a wound bacillus but Gram-negative in old cultures. Similarly, *Clostridium Chauvoei*, the causative organism of quarter-evil was known before 1921 as Gram-positive in the tissues and usually Gram-negative in culture.

Beef-extract broth is made to a composition unfamiliar in this country. [It is, however, printed in the formula for the basic broth used for the standard agar in the tests for graded milk (ANALYST, 1929, 235.)] It omits addition of salt, and adds: "Earlier investigators added salt to this medium. It is not used to-day." The usual practice in this country has been and, I believe, largely is, to use five or ten grammes of salt to the litre. English formulae demand ten or twenty grammes of Lemco, but for very many years American workers have used three grammes of "beef extract" to the litre, sometimes specifying Lemco, sometimes not. Peptone is, similarly, reduced from twenty or ten grammes to five grammes per litre. However, Professor Tanner does not support the claims of such broth on the ancient plea, for which something can be said, that no later adjustment of reaction is usually necessary.

The use of white of egg for clarifying media is a very old device that meets with approval by most workers in this country and by some eminent Americans.

Professor Tanner says "this is not good practice, since it is known that egg contributes materials to the medium. Those who use egg in this manner prepare an egg agar, egg gelatin, etc. They do not secure a standard agar or gelatin medium." This seems to introduce the debateable points, firstly, whether a medium from which the coagulable part of egg has been removed by filtration can claim to be an egg medium, and, secondly, having regard to the invariably good results obtained with egg-clarified media for so many years, whether change of name would be preferable to change of practice.

The author avoids, as much as possible, the use of pathogenic bacteria in teaching, since "the continued study of pathogens tends to give a new student a warped idea of the science."

WILLIAM PARTRIDGE.

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY. Vol. IX. By J. W. MELLOR, D.Sc., F.R.S. Pp. 967. London: Longmans, Green & Co. 1929. Price 63s. net.

The ninth volume of Mellor's compendious treatise deals with arsenic, antimony, bismuth, vanadium, columbium and tantalum. The treatise has now come to be regarded as an essential part of a chemical library, and chemists eagerly look forward with every confidence to the publication of the remaining volumes.

The new volume bears the characteristic traits of all Dr. Mellor's books, namely, systematic arrangement, exhaustiveness and completeness. Yet, despite his untiring and, indeed, superhuman energy in searching the vast chemical literature, apparently never missing a single important point, and then recording it all with astounding exactitude, we find that he has been able to find space, here and there, to give us many human touches. Thus the sections devoted to the historical and physiological aspects of arsenic and antimony compounds are particularly interesting, and might well be reserved for leisure reading.

Considered as a whole, the available and somewhat unwieldly matter has been assimilated and recorded in due perspective with regard to its importance. It must be confessed, however, that it is irritating to be continually confronted with almost barren phrases to the effect that X discussed this, and Y did that, without any indication as to their conclusions. This, perhaps, is inevitable in a comprehensive treatise of the size of Mellor's. Full references are included.

Dr. Mellor still hangs on tenaciously and slavishly to his nomenclature of inorganic substances, whether they be compounds or not. Fewer meaningless graphical formulae, however, are to be found in the present volume than in the earlier volumes.

The volume has been published in the usual satisfactory manner, and the proof-correcting seems to have been very thorough; only two misprints were seen, namely, "Rd." for "Radium," and an effect usually attributed to Thomson is coupled with the name of Thompson.

In conclusion, Dr. Mellor is to be heartily congratulated on the publication of yet another volume of his invaluable treatise, and must also be accorded the warmest appreciation and thanks of chemists on the great assistance he is continuing to render.

HUBERT T. S. BRITTON.

AMERICAN SOAP-MAKER'S GUIDE. AN UP-TO-DATE TREATISE ON THE ART AND SCIENCE OF THE MANUFACTURE OF SOAPS, CANDLES, AND ALLIED TOILET PREPARATIONS. By I. V. STANLEY STANISLAUS and P. B. MEERBOTT. Pp. 709. 105 Illustrations. London: Chapman & Hall, Ltd. 1929. 50s. net.

Described as "the most complete and exhaustive book in the English language," this book, while largely re-written and considerably expanded, is based partly on the second edition of Brannt's well-known "Soap-Makers' Handbook," published in 1912. It opens with a very interesting historical review of the soap industry from its earliest beginning to the present day, and then follows very much the usual conventional lines, the next eight chapters dealing with the constitution and properties of oils, and soaps, the more important fats and oils used, their preparation, bleaching and refining, and methods of examination. The simple triglycerides are still stated to form the preponderating constituents of oils and fats, and the conclusions of Hilditch in this country, and of Bömer and Ebach in Germany, that natural fats and oils consist mainly of mixed glycerides are ignored. The modern views as to the nature of soaps and soap solutions are well discussed, and the work of MacBain is given due recognition, but the erroneous statement in the previous edition that soaps are *soluble* in ether, benzol, and petroleum spirit, is here repeated. There is a very good and well illustrated description of modern methods of fat rendering, but the preparation of oils and fats by expression and extraction receives very scanty treatment. The section dealing with bleaching and refining has not been altered from the last edition, and was already out of date in 1912; even the mistake of calling bleaching powder *calcium chloride* has not been rectified. A chapter on Sulphonated and Hydrogenated Oils deals chiefly with the preparation, constitution, and analysis of sulphonated oils, hydrogenated oils being dismissed in about one page. Juillard's work on sulphonated oils is fully described, but nearly all the formulae he assigns to the products are wrongly quoted, and his name is misspelt Julliard (incidentally it occurs in the index as Juliard). Soap made from hydrogenated fish or whale oil is stated to have sometimes a slight fishy odour, this being less noticeable as the iodine value of the oil falls from 58° to 55° C. One chapter describes a number of suggested substitutes for fatty acids and soaps, emanating principally from Germany, and including several sulpho-derivatives; throughout this chapter the term carbohydrate is used where hydrocarbon is obviously intended. Thus tetralin, tetrahydronaphthalene, is quite wrongly referred to as a "partially hydrated carbohydrate."

For some unexplained reason there are two chapters on the analysis of oils, one headed Examination of Fats and Oils, the other General Tests for determining the Purity of Oils. Some processes, *e.g.* saponification value, and iodine value, are described in both, the former being dealt with at great length, and including four pages taken verbatim from a paper by A. H. Allen before this Society as long ago as 1886. The time recommended for saponification, *viz.* 10–20 minutes, would hardly be sufficient in the case of many oils, and 1 c.c. of $N/2$ KOH solution is wrongly stated to contain 280 mgrms. of potassium hydroxide. The only method given for determining the iodine value is that of Hübl, no reference being made to either the Wijs or the Hanus process. Many of the tests given are quite obsolete, such as testing for free fatty acids by pouring an oil on to cuprous oxide, and the determination of glycerin by oxidation with potassium permanganate in a strongly alkaline solution, which is said to be "the most reliable process." At the same time many important tests are not even mentioned, *e.g.* the refractive index, Halphen's test for cottonseed oil and Bellier's test for arachis oil, and the description of "solid foreign substances, such as fragments of skin, parts of plant, dirt, etc.," as unsaponifiable matter is quite incorrect according to the present day acceptation of this term.

There follow three chapters on the alkalis and their examination, water supply, lime for causticising alkali, and common salt. A well-illustrated chapter next describes soap pans, frames, crutchers, and other apparatus used in soap-making, and a good outline is then given of the various processes of soap manufacture, glycerin recovery and distillation being briefly dealt with under the process of soap-boiling. The seven following chapters describe, with formulae, the manufacture of the different qualities of household soap, both hard and soft, genuine and filled, textile soaps, washing powders, toilet soap (cold process, re-melted and milled), medicated soaps and shaving soaps. Some of the formulae appear rather unworkable, but these chapters give much useful information. One of the most important developments of recent times in the soap industry is the use of soap-coolers in place of frames, and it is surprising to find no reference to this subject, while other notable omissions are references to the manufacture of soap flakes and the use of per-salts in soap powders. The chapter on soap analysis has been brought more up to date, and gives methods for all the more important determinations. Some obsolete methods are still retained, and there is no reference to McNicol's method of determining rosin, which is now being officially adopted in this country. The only process for the determination of phenols is that found in most text-books, and attributed to Lewkowitsch, of salting out the soap from a strongly alkaline solution, filtering, concentrating the filtrate to small bulk, and acidifying in a graduated tube, in which the separated phenols may be read off. This method appears to have been quite generally abandoned in favour of precipitation of the phenols from their solution with a bromide and bromate solution standardised against a similar type of phenol. The determination of total fatty and rosin acids is detailed at length twice over, and it is out of place to find in this

chapter a test for unsaponifiable matter in an oil, twice repeated in almost identical terms, though first described as qualitative, and then as quantitative.

The essential oils and other materials used for perfuming soaps, and their method of compounding are dealt with in three following chapters, and here many of the mistakes of the last edition have been rectified. Some mis-statements, however, still appear, as with the specific gravity of bergamot oil, which is said to lie between 0·856 and 0·888, although the usually accepted limits are 0·880 to 0·886, and Bourbon geranium oil is quite erroneously stated to be obtained in the Presidency of Bombay from *Andropogon schoenanthus*, though in fact it is a true geranium or pelargonium oil emanating from the island of Rèunion (Bourbon).

There is a short chapter on candle materials and manufacture, the latter being confined to a description of moulding only, and there are two more dealing with Toilet Creams and Dentifrices, these last consisting mainly of verbatim extracts, with the scantiest acknowledgment, from an English book on these subjects reviewed in this Journal a short time ago.

The book is well printed, and many of the illustrations are good, much better than in the last edition, but it has been compiled and passed for publication in an extraordinarily careless manner, possibly due to lack of proper collaboration between the two authors. In some cases whole paragraphs are repeated twice, and in many others they are inserted in the midst of quite irrelevant matter, whilst the number of misprints is astonishing. It can only be regarded both in its matter, and the manner of presentation, as a most disappointing book.

W. H. SIMMONS.

Publications Received.

THE PYROLYSIS OF CARBON COMPOUNDS. By C. D. HURD. New York: The Chemical Catalog Co., Inc. Price $12.50.

THE CHEMISTS' YEAR BOOK, 1929. Edited by F. W. ATACK, R. T. ELWORTHY, and F. M. TURNER. Manchester: Sherratt & Hughes.

INDUSTRIAL CARBON. By C. L. MANTELL. London: Chapman & Hall. Price 21s. net.

ANLEITUNG ZUR ORGANISCHEN QUALITATIVEN ANALYSE. 2nd Edition. Berlin: Springer. Price 6.60 R. marks.

POLAR MOLECULES. By P. DEBYE. New York: The Chemical Catalog Co., Inc. Price $3.50.