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Locust-Kernel Gum and Oil.

By A. L. WILLIAMS, A.I.C.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, May 2, 1928.)

The preparation of a mucilaginous substance from the endosperm of the locust or carob bean (*Ceratonia siliqua*), has been the subject of a number of patents. In all cases the mucilage is extracted from the endosperm by hot water, and the various patents relate to different methods of obtaining the endosperm free from the tenacious husk so as to yield a product free from colour.

According to the most recent English patent (No. 241,186 of 1925), the seeds are separated from their shells by submitting them to rollers and crushers. The endosperms are then heated in a rotary oven until they attain a golden brown colour. They are thrown into about twenty times their weight of boiling water, in which they are stirred. The viscous mixture is pumped to a filter or to sieve machines, and the clear filtered product is dried in a hot-air drier. The dried product is then finely ground.

The substance is to be obtained commercially as a nearly white powder under the names "Locust-Kernel Gum" and "Gum Tragon," and also as a tough jelly, containing about 4 per cent. solids, under the name "Tragasol."

Composition of the Gum.—The composition of the endosperm of the locust bean has been studied by Effront (*Compt. rend.*, 1897, **125**, 38), who isolated from it a carbohydrate, caroubin, which had the same composition as cellulose,

and gave extremely viscous solutions with water. He claimed (*Compt. rend.*, **1897, 125**, 309) that it yielded a new sugar, caroubinose, on hydrolysis with dilute acid, but van Ekenstein has stated (*Compt. rend.*, 1897, **125**, 719) that this sugar is identical with dextro-mannose.

According to Bourquelot and Herissey (*Compt. rend.*, **1899, 129**, 228, 391), by hydrolysing the endosperm with 4 per cent. sulphuric acid at 110° C. a mixture of mannose and galactose is obtained in the proportion of 83·5 per cent. of mannose and 16·5 per cent. of galactose. A certain amount of insoluble matter, on hydrolysis with stronger sulphuric acid, yields mannose only. The hexoses are present as anhydrides, *i.e.* as mannans and galactans, chiefly as hemicellulose.

The composition of the endosperm of the locust bean and that of the extracted gum ("Tragon") is shown by the following analyses:*

	Galactan.	Mannan.	Pentosans.	Proteins.	Nitrogen	Cellular Tissue.	Mineral matter.	Laevulan.
Endosperm, per cent.	29·18	58·42	2·75	5·29	0·83	3·64	0·82	trace
"Tragon," ,, ,,	24·84	64·39	4·07	2·40	0·39	1·46	2·81	,,

The ultimate composition of the gum, calculated on the ash-free substance, is: Carbon, 44·17; hydrogen, 6·32; oxygen, 49·11; and nitrogen, 0·40 per cent.

This practically agrees with a formula of $C_6H_{10}O_5$; so that, whereas the true gums, *e.g.* gum arabic or gum tragacanth, are acids of high molecular weight—a combination of a nucleus acid with various hexoses, pentoses, etc.—the gum obtained from the locust bean is a carbohydrate composed of the anhydrides of the hexoses mannose and galactose, and probably of that peculiar class of substances, the hemicelluloses.

PROPERTIES.—The gum swells in cold water and, on stirring, separates into lumps which do not break down readily. It must be allowed to stand for a considerable time before the lumps absorb sufficient water to form a homogeneous mixture. Solution is best effected by adding cold water, at the same time stirring vigorously, and boiling until a smooth homogeneous mixture is obtained. Water is then added in small quantities at a time, care being taken to prevent the formation of lumps. I have found this tendency to form lumps more pronounced in a sample bought under the name "Locust-Kernel Gum," than in "Gum Tragon."

An opaque, tasteless and odourless mucilage is thus obtained. The jelly "Tragasol" yields a clear mucilage; it contains a phenolic antiseptic. As an adhesive it is similar to starch solution.

REACTIONS OF THE GUM.—Basic salts precipitate the gum complex, a heavy white gelatinous precipitate being produced by basic lead acetate. Normal salts have little action, except in concentrated solutions, when the gum complex is precipitated.

The gum does not reduce Fehling's solution, but yields a blue gelatinous precipitate, soluble in dilute acids.

* Publications of the Tragasol Products Ltd. (1926).

Acids, especially mineral acids, lower the viscosity, but boric acid renders the mucilage more viscous.

Borax has this property to a marked degree. A saturated solution of borax will convert a 0·5 per cent. solution of the gum into a solid jelly.

Alkalis increase the viscosity, especially of strong solutions, which become glutinous, and at the same time the colour is darkened.

Alcohol precipitates the gum complex in the form of a white flocculent gelatinous mass.

REACTION WITH TANNIN.—When a dilute solution of tannin is carefully added to a solution of the gum, the gum becomes first more viscous, then thin and milky, and, finally, on adding an excess of tannin a soft gelatinous mass separates. After standing for some time the gel shrinks, taking the form of the vessel containing it, and finally separates into a white or buff-coloured clot (according to the colour of the tannin), and a clear supernatant liquid. On warming to a temperature of 40–50° C. the whole becomes a homogeneous, highly viscous, turbid mucilage with strong solutions, and a clear liquid with dilute solutions. The precipitate separates again on cooling. This change on heating and cooling is strictly reversible.

The precipitate is also dispersed by solutions of sodium benzoate, potassium thiocyanate, alkalis, and particularly by substances which contain a large number of hydroxyl groups, *e.g.* glycerol, sugars.

This precipitation with tannin occurs in acid but not in alkaline solutions; it does not take place in the presence of acetic acid.

Some of the tannin is removed from the precipitate by washing with water, and the whole of it by alcohol, leaving the hexosan complex in a flocculent form which can be readily dissolved in water to produce the original mucilage.

USES IN INDUSTRY.—The reaction with tannin is of value in leather manufacture. The gum acts as a restraining agent in the tanning process; strong astringent liquors may be used in order to carry out the process with greater rapidity and without detriment to the product (Greenwood, Eng. Patent 5018 of 1910, 7635 of 1915). The hexosan-tannin precipitate is to be obtained commercially for this purpose under the trade name "Cutiloid."

Owing to the high viscosity and the property of reverting to a continuous, unbroken film on drying, the gum is used in the sizing and finishing of yarns; it is also used for thickening the colour paste in calico printing.

It has recently been introduced into food as a thickener for sauce, and it seems probable that other uses will be found for such a tasteless, odourless, colourless and highly viscous mucilage. Its price is about one-tenth that of gum tragacanth.

The samples which I examined were free from arsenic and lead.

DETECTION.—The reactions with tannin, borax and Fehling's solutions are, apparently, the most characteristic. In the following table the action of these

reagents on locust-kernel gum and a few substances which also yield viscous solutions is compared:

	Tannin Solution.	*Borax Solution.*	*Fehling's Solution.*
Locust-kernel gum.	With excess of reagent. Buff coloured clot precipitated. Clear, supernatant layer. Dispersed on warming, reappears on cooling. Dispersed by glycerin, sugar, etc. Precipitate, after washing with alcohol dissolves in water, producing the original mucilage.	A solid jelly formed. Liquified by excess of borax solution or acids.	Blue gelatinous mass precipitated. Soluble in acids.
Gum tragacanth.	No action.	No action.	No action.
Gum arabic.	No action.	No action.	No action.
Dextrin.	Turbidity with strong solutions. No change on warming.	No action.	No action.
Gelatin.	White precipitate. No change on warming.	No action.	No precipitate. Violet coloration.
Agar-agar.	Turbidity remains in suspension. Dispersed on warming, returns on cooling.	No action.	No action.
Starch solution.	Turbidity with strong solutions. Dissolves on dilution with water.	No action.	No action.

Locust-kernel gum gives no colour with iodine.

SEPARATION FROM SAUCE.—A sample of sauce which contained 1 per cent. of the gum was examined in the following manner:

About 50 grms. of the sauce were diluted with an equal volume of water, boiled and filtered through glass wool. The filtrate was concentrated to a syrup, and 50 c.c. of alcohol added. A flocculent precipitate was produced; it was separated and dissolved in water. On adding excess of tannin solution the precipitate produced had not the characteristic appearance of that obtained with locust-kernel gum. It was separated, washed once by decantation with cold water, and then shaken with alcohol. The flocculent insoluble matter was filtered off, dissolved in water and again precipitated by excess of alcohol. The precipitate was separated and dissolved in water.

In this way a fairly pure mucilage was obtained. It gave the characteristic precipitate with tannin, the gelatinous precipitate with Fehling's solution, and, when concentrated to the consistency of, say, glycerin, gave the characteristic jelly with a saturated solution of borax.

The same treatment proved to be satisfactory for separating the locust-kernel gum from jam.

Quantitatively, the separation is unsatisfactory, not more than 75 per cent. of the gum being recovered. Attempts to use the precipitate with Fehling's solution, for quantitative purposes, were also unsuccessful, although the original

mucilage may be recovered from it by carefully dissolving it in cold dilute hydrochloric acid and precipitating the gum with alcohol.

Locust Kernel Oil.

I have been unable to discover any records of the analytical values of this oil. When extracted with ether the ground kernels yielded a dark green oil which gave the following figures:

	Sp. gr. 15·5° C.	Butyro-refracto-meter reading at 40° C.	Iodine value (Wijs).	Saponification value.	Insoluble fatty acids. Per Cent.	Reichert–Meissl value.	Polenske value.	Unsaponifiable matter. Per cent.
Old kernels	0·950	65·0	98·5	205·5	86·5	—	—	—
Fresh kernels	0·951	65·0	99·1	198·0	87·4	1·8	0·8	2·86

Insoluble Fatty Acids.

	Titre test.	Iodine value (Wijs).	Neutralisation value.
Old kernels	25·4–25·7° C.	101·7	183·2
Fresh kernels	25·2–25·6° C.	100·5	184·5

The fact that the neutralisation value of the fatty acids is lower than the saponification value of the oil seems to point to the presence of soluble (non-volatile) fatty acids of high molecular weight. The oil gave a negative result for vitamin *A* when submitted to the antimony trichloride test.

The ground kernels from which the oil had been extracted had the following composition:

Water	12·08 per cent.
Ash	2·80 ,,
Oil	1·80 ,,
Albuminoids	15·12 ,,
Fibre	6·10 ,,
Carbohydrates (by difference)	62·10 ,,
	100·00

The writer is indebted to the Birmingham Public Health Committee for the use of the Municipal Laboratory and to Mr. C. A. Mitchell for samples.

LIST OF PATENTS ON THE MANUFACTURE OF LOCUST KERNEL GUM.

English Patents Nos.—567 of 1857; 8793 of 1893; 13345 of 1894; 24877 of 1894; 27186 of 1903; 10822 of 1905; 569 of 1908; 19768 of 1909; 10075 of 1910; 20648 of 1911; 564 of 1912; 2756 of 1912; 15783 and 15860 of 1912; 13508 of 1913; 241,186 of 1925.

City Analyst's Department,
44, Broad Street, Birmingham.

The Detection of Iso-propyl Alcohol.

By DOUGLAS HENVILLE, F.I.C.

In a number of cases of drunkenness which came before the Magistrate at the Old Street Police Court in the latter part of 1927 it was stated that more than the usual deleterious effects were suffered by the defendants, who blamed a certain class of wine, described as "Port" or "Red Wine," sold in the district.

At the request of the Ministry of Health samples of these wines were taken, under the Food and Drugs Acts, from publicans in the district, and the wines were examined for the presence of any deleterious substances and for the possible presence of methyl or iso-propyl alcohols which might have been substituted for, or added to, the ethyl alcohol normally present. On analysis the samples were found to be sweet wines of port type, and to be free from any deleterious substances, methyl alcohol (methylated spirits) or iso-propyl alcohol.

Early this year it was found that industrial methylated spirits were being sold in the district for drinking purposes, and it was from this cause, and not from the wines, that the harmful effects had been experienced.

The examination of the wines for the presence of methylated spirits was carried out by the method of Denigès as modified by Simmonds (Analyst, **1912, 37, 16**), and later by G. C. Jones (Analyst, **1915, 40, 218**).

It was necessary to devise a method for the detection of iso-propyl alcohol in the presence of ethyl alcohol. Iso-propyl alcohol has a characteristic smell even when highly diluted. It boils at 82·7° C., has a sp. gr. of 0·7897 ($\frac{15\cdot6°C}{15\cdot6°C}$), and forms, with water, a constant-boiling mixture which boils at 80·4° C.

The Detection of Acetone.—The most hopeful method of detecting iso-propyl alcohol appeared to be by oxidising it into acetone and proving the presence of this compound.

Two tests given for detecting the presence of acetone in urine are:

(1) A strong solution of sodium nitro-prusside is added to the urine, which is then made alkaline with potassium hydroxide. In the presence of acetone a red colour is formed which changes to violet with acetic acid.

(2) A strong solution of sodium nitro-prusside is added to the urine, followed by solution of ammonia, when a brilliant violet colour is obtained if acetone is present.

Experiments carried out to determine the relative sensitiveness of these tests showed that the first easily detected 0·001 ml. of acetone in 2 ml. of water and that the second would detect 0·05 ml. of acetone in 2 ml. of water.

Further experiments showed that, although both tests gave negative reactions with methyl alcohol, iso-propyl alcohol, formaldehyde and ethyl alcohol, the more sensitive potassium hydroxide test gave a strong positive result with acetaldehyde, while the ammonia test gave a negative result.

The potassium hydroxide test, therefore, could not be used, and it was essential that the ammonia test should be more sensitive if it were to be of use.

Squire describes a test for acetone in urine as follows:—" A measured quantity of 15 ml. of the sample is mixed with 0·5 to 1·0 ml. of glacial acetic acid and a drop of fresh sodium nitro-prusside solution. One ml. of strong ammonia is run on the surface, and, if acetone is present, a purplish violet ring appears at the line of contact. It is stated that 1/400 per cent. of acetone can be detected."

The sensitiveness of the sodium nitroprusside and ammonia test, with and without a first addition of acetic acid, was compared, and it was found that the presence of acetic acid increased the sensitiveness so far that 0·005 ml. of acetone could be detected. In these tests the volume of liquid containing the acetone was maintained at 2 ml., this quantity being increased to about 8 ml. by the addition of the reagents. The tests were carried out in small narrow beakers with a capacity about 14 ml. When testing liquids containing small quantities of acetone the colour appears after some few minutes' standing, and then deepens to a characteristic and definite shade.

It was further found, when distilling alcoholic liquids containing small quantities of acetone and testing 2 ml. of distillate, that the presence of ethyl alcohol considerably reduces the sensitiveness of the test.

THE OXIDATION OF ISO-PROPYL ALCOHOL.—In preparing the test for detecting the presence of methylated spirits a 10 per cent. alcoholic solution of the sample, after distillation, must be made. This solution may be conveniently used for the detection of iso-propyl alcohol, and the following experiments were made:

Ten per cent. alcoholic solutions containing, respectively, 1 per cent., 0·3 per cent., 0·2 per cent., and 0·1 per cent. of iso-propyl alcohol were made up.

Ten ml. of these solutions containing, respectively, 0·1 ml., 0·03 ml., 0·02 ml., and 0·01 ml. of iso-propyl alcohol were taken for oxidation.

In each case the 10 ml. quantity was oxidised with potassium dichromate and sulphuric acid, the mixture distilled, and the first 2 ml. of distillate tested for acetone.

Strong positive reactions were obtained with the distillates from the liquids originally containing 0·1 ml. and 0·03 ml. of iso-propyl alcohol; a weaker but definite reaction was obtained in the case of the distillate from the 0·02 ml. quantity, and the distillate from the 0·01 ml. quantity, after standing 10 minutes, showed a pale pink but definite colour. A blank experiment was carried out, 10 ml. of a 10 per cent. solution of the ethyl alcohol being used throughout, and a negative reaction was obtained.

Supposing, therefore, that the original sample before distillation contained 10 per cent. of alcohol by volume, the test will detect 0·1 per cent. of isopropyl alcohol.

When small quantities of iso-propyl alcohol are oxidised and distilled, all the acetone produced is found in the first 2 ml. of distillate collected. This was not found to be the case when quantities of 0·5 ml. and 1·0 ml. of iso-propyl alcohol were oxidised and distilled.

The complete test is carried out as follows:

(1) Ten ml. of water are placed in a narrow-necked flask, having a capacity of about 120 ml., 5 ml. of concentrated sulphuric acid added, and the mixture cooled. Ten ml. of the 10 per cent. alcoholic solution prepared for the methylated spirit test are run in, and the whole mixed. Three grms. of powdered potassium dichromate are added, and the flask at once attached to a small condenser. The contents of the flask are shaken round so as to dissolve the dichromate (there is a considerable rise in temperature), and the liquid is allowed to stand for about 5 minutes and then distilled, the first 2 ml. of distillate being collected in the small beaker in which the test for acetone is to be made.

(2) To the 2 ml. of distillate are added 2 ml. of water and about 1 ml. of acetic acid (B.P.), followed by two to three drops of a strong freshly-made solution of sodium nitroprusside, the liquid being mixed after the addition of each reagent. Ammonia solution is then added in excess to a total volume of about 8 ml. and the liquid mixed. In the presence of acetone a violet coloration is obtained, either at once or on standing, according to the amount of acetone present.

NOTE.—Methylated spirits contain acetone in small quantities. The acetone is derived from the wood naphtha which is used as a denaturant. Industrial methylated spirits will contain about 0·5 per cent., or less, of acetone.

STEPNEY BOROUGH CHEMICAL LABORATORY,
43, WHITE HORSE STREET, E.1.

The Identification of the Prohibited Coal Tar Colours in Foodstuffs.

BY A. R. JAMIESON, B.Sc., A.I.C., AND C. M. KEYWORTH, M.Sc., F.I.C.

VARIOUS schemes have been formulated for the detection of artificial colouring matter in foodstuffs, but the introduction of legislation prohibiting the use of certain colours has made it imperative that reliable methods should be available for the detection of the five synthetic dyestuffs scheduled in the Public Health (Preservatives, etc., in Food) Regulations, 1925.

These dyes are Picric Acid (7), Victoria Yellow (8), Martius Yellow (9), Aurantia (12), and Aurine (724).*

It is difficult to find in the existing schemes for the detection of dyestuffs a method which will enable one to identify with certainty the presence in food of the prohibited dyestuffs, although Nicholls has recently published a scheme for the separation and identification of these colours, and he also gives particulars of their chemical properties (ANALYST, 1927, **52**, 585).

We have found that the prohibited dyestuffs give, with certain reagents, sparingly soluble crystalline precipitates. These crystalline precipitates present

* The numbers in brackets refer to the number in the Colour Index of the Society of Dyers an Colourists, 1924.

such distinctive microscopical appearances as to provide a reliable method for the identification of the particular dyestuff. Certain new colour reactions are also indicated.

In colouring either food or drink artificially, the dyestuff is used in minute quantities. According to the Final Report of the Departmental Committee on the Use of Preservatives and Colouring Matters in Food, the amount of dyestuff used varies from 1 part in 2000 parts of food to 1 part in 30,000 or even 500,000 in mineral waters (page 49, par. 177).

With such dilutions many of the usual distinctive reactions of dyestuffs are not effective. (*Cf.* Reactions of Dyes on the Fibre, Keyworth, *J. Soc. Dyers & Colourists*, **1927**, **43**, **343**.) In the case of extremely dilute solutions it would obviously be advisable to concentrate the solution before attempting to identify the dye by the formation of distinctive crystalline precipitates.

We found that with suitable reagents picric acid, Martius yellow and aurantia give characteristic and distinctive crystals. Victoria yellow and aurine showed a marked reluctance to form crystalline precipitates, but we have included in our scheme two useful tests for their detection.

The crystalline precipitates are formed and the colour reactions for Victoria yellow and aurine are given with a dilution of 1 in 10,000 of dyestuffs, and, in some cases, it has been found possible to detect the dyes at a dilution of 1 in 50,000.

In making these tests only a very small quantity of the dye solution is required, and satisfactory and definite results have been obtained when working with 5 drops from a 1 c.c. pipette (0·20 c.c.) of the solution, the dilution being 1 in 10,000.

The dye present in any foodstuff is extracted according to the methods given in *Allen's Commercial Organic Analysis* (5th Ed., 1927, Vol. V, p. 431–4), and concentrated as far as possible.

Before proceeding to a detailed examination of the dyestuff it should be borne in mind that all the prohibited synthetic colours dye wool yellow from a weak acid bath. The preliminary test suggested by Nicholls (*loc. cit.*) can be used with advantage to show the presence of the prohibited colours.

Many of the yellow and orange dyestuffs contain sulphonic acid groups, and the presence of these groups renders the dyestuff non-toxic (*cf. Ministry of Health, Final Report of the Departmental Committee on the Use of Preservatives and Colouring Matters in Food*, p. 51, par. 184. It is necessary, therefore, to distinguish these from the prohibited dyestuffs which contain no sulphonic acid groups. Moreover, the total number of unsulphonated nitro dyes is very small, and, since four of the prohibited dyes are nitro dyes, unsulphonated, the first step is to find whether the yellow dye belongs to this group or not. It may be possible to dispense with this preliminary test for sulphonation, but at the moment we have not examined *all* the *sulphonated* nitro dyes to determine whether it is possible to obtain crystals similar to those given by the unsulphonated nitro dyes with the specific reagents. Consequently it is advisable to apply the preliminary test for sulphonation, and if the nitro dye is unsulphonated then the

crystals obtained are specific for the dye in question. In order to determine whether the dye is sulphonated or not, a portion of the extract is warmed with stannous chloride and hydrochloric acid until partly reduced, then neutralised with potassium hydroxide, when the nitro dyes assume a brownish-red colour (*cf.* A. G. Rota, *Chem. Ztg.*, 1898, 437–442; ANALYST, 1899, **24**, 41). The coloured solution is now treated with ether, and if, after shaking, the colour does not pass to the ethereal layer, the solution is acidified with acetic acid, again shaken, and the effect on the coloured layer noted. In the case of nitro dyes the colour passes to the ethereal layer, but in the case of sulphonated nitro dyes the colour does not pass to that layer, either in presence of acid or alkali.

The results of our experimental work on the formation of crystalline precipitates are given in Table I, the reagents employed and their strength being as undernoted:

	Strength of solution.		Strength of solution.
Berberine sulphate	0·25 per cent.	Acetic acid	normal
Gold chloride ..	2·0 ,, ,,	Potassium hydroxide	,,
Phosphotungstic acid	10 ,, ,,	Dilute ammonia ..	0·2 per cent.
Silicotungstic acid ..	10 ,, ,,	Chrome alum	5 ,, ,,
Silver nitrate ..	5 ,, ,,	Potassium cyanide ..	5 ,, ,,
Stannous chloride ..	3 ,, ,,	Wijs iodine chloride solution (1/5 *N*)	
Dilute hydrochloric acid	3 ,, ,,		

In Table II are detailed the results of our experiments to produce characteristic and confirmatory colour reactions. The reagents used and their strength are detailed below:

Calcium hypochlorite (sp. gr. 1·005)+2 c.c. of glacial acetic acid per litre.
Hydrosulphite powder (10 per cent. solution).
Hydrosulphite B. (For preparation see Keyworth, *loc. cit.*)
Hydrosulphite R.S. (,, ,, ,, ,, ,,)

The following is a summary of the most important results obtained:

PICRIC ACID.—Five drops (0·2 c.c.) of a solution of 1/10,000 gave characteristic yellow rosettes (Fig. 1) when treated with 1 drop of berberine sulphate solution. A number of other alkaloids also gave crystalline precipitates, but these were not sufficiently characteristic. Potassium cyanide gives a confirmatory specific reaction, *viz.* a brown coloration on warming.

MARTIUS YELLOW.—Five drops (0·2 c.c.) of a solution of 1/10,000 gave characteristic crystals, large yellow needles occasionally in clusters (Fig. 2) when treated with 1 drop of berberine sulphate solution. It was also found that 1 drop of gold chloride gave distinctive crystals—fine yellow needles (Fig. 3). Interesting crystals (Fig. 4) were also obtained by the addition of 2 drops of silver nitrate solution (tufts of very fine brownish-red needles). These crystals were difficult to photograph, being apparently decomposed by the light from the carbon arc used as an illuminant. This difficulty was overcome by photographing them

Fig. 1.
Picric acid and
Berberine sulphate.

Fig. 2.
Martius yellow and
Berberine sulphate.

Fig. 3.
Martius yellow and
Gold chloride.

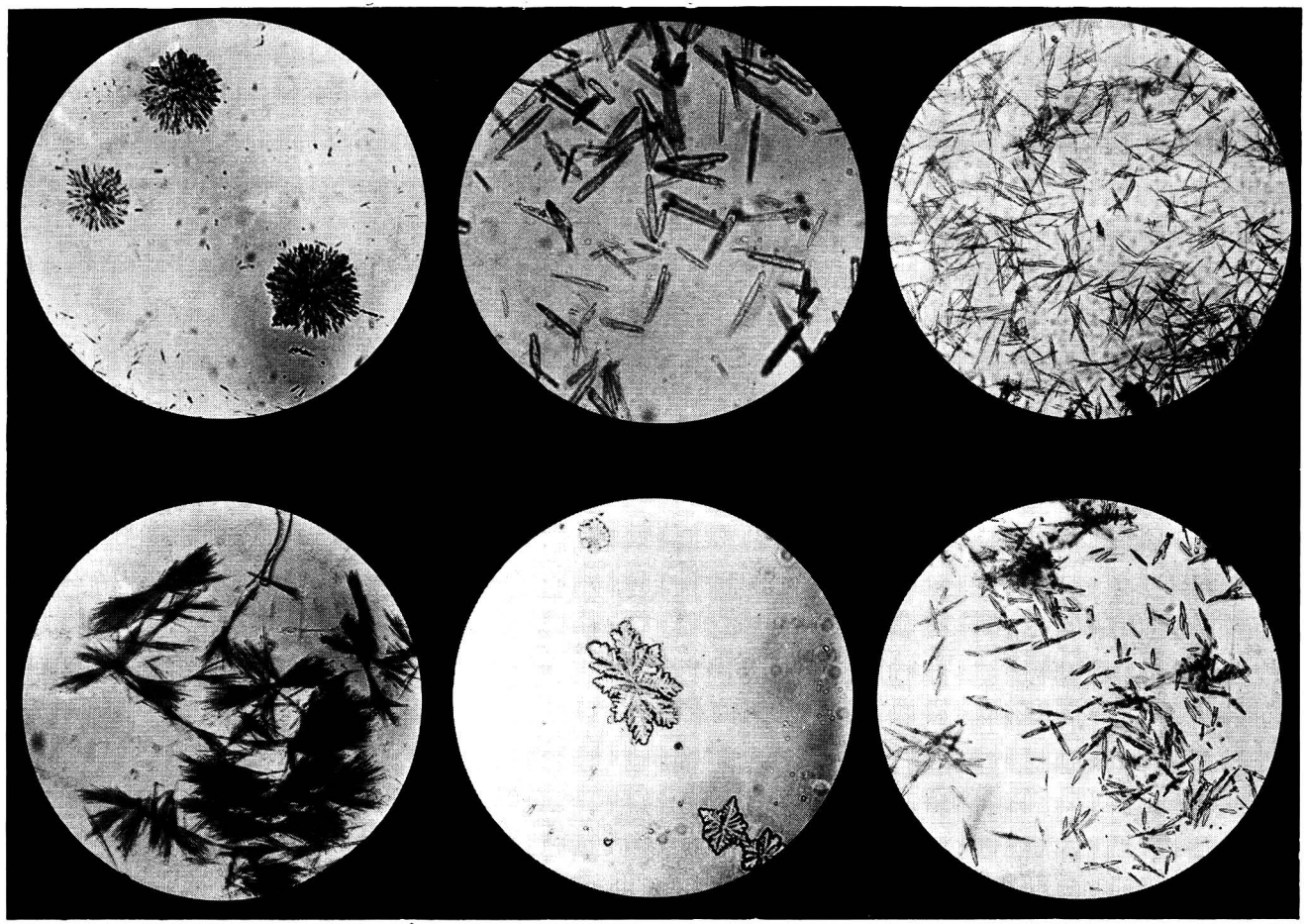

Fig. 4.
Martius yellow and
Silver nitrate.

Fig. 5.
Aurantia and
Phosphotungstic acid.

Fig. 6.
Aurantia and
Silicotungstic acid.

(*All* × 250).

TABLE I.

Dyes.	*Berberine sulphate.*	*Phospho-tungstic acid.*	*Silico-tungstic acid.*	*Chrome alum.*	*Zinc + HCl.*	*Gold chloride.*
Aurine.	N.C.	Yellow col. No ppt.	Yellow col. No ppt.	Red lake. X	Decol.	Decol. with red A.P.
Aurantia.	Faint ppt.	Decol. with C.P. X	Decol. with C.P. X	Decol. with ppt.	Decol., faint ppt.	Decol. with ppt.
Martius yellow	C.P. X	Decol. with A.P.	Decol. with A.P.	Decol. with A.P.	Decol.	C.P. X
Picric acid	C.P. X	N.C.	N.C.	N.C.	Decol.	N.C.
Victoria yellow	N.C.	Decol.	Decol.	Decol.	Pink colour. X	Decol.

TABLE II.

Dyes.	*Sodium bisulphite.*	*Sodium persulphate.*	*Oxalic acid.*	*Hydrosulphite 10 per cent. soln.*	*Hydrosulphite "B."*	*Hydrosulphite R.S.*	*Calcium hypochlorite soln.*	*Rhodamine "B."*
Aurine.	Decol. returns with H_2O_2.	Yellow.	Yellow.	Decol., returns with H_2O_2.	Pink. No change with H_2O_2.	Pink –> cherry red with H_2O_2.	Decol.	No immediate ppt.
Aurantia	Slightly darker, then –> original.	Decol. Col. returns on warming, then decolorised.	Pale opalescence, yellowish soln. Yellow when hot.	Decol. –> Pink.	Decol. N.C. with H_2O_2.	Darker –> decol. N.C. with H_2O_2.	L.C.	No immediate ppt.
Martius yellow.	N.C.	Decol. with opalescence, Col. returns on warming –> decol.	Yellowish opalescence. Yellow soln. when hot.	Decol. –> Brown.	Brown –> pink. L.C. with H_2O_2.	Brownish red –> gradually decol. –> pale yellow. Darkens with H_2O_2.	Decol.	No immediate ppt.
Picric acid.	N.C.	N.C.	N.C.	Decol.	Dark brown, pink with H_2O_2.	Deep reddish brown. L.C. with H_2O_2.	L.C.	Immediate pink ppt.
Victoria yellow.	N.C.	Decol. Faint yellow on warming, then decol.	Decol.	Decol.	Orange brown. L.C. with H_2O_2.	Orange brown.	Decol.	No immediate ppt.

ABBREVIATIONS.—"Col."—Colour; "Decol."—Decolorised; "A.P."—Amorphous precipitate; "C.P."—Crystalline precipitate; "X"—Specific test; "N.C."—No change; "L.C."—Little change; "–> "—Changing into.

through a brown screen. The test with berberine sulphate was the most sensitive of the three and is the one recommended.

AURANTIA.—Five drops of dyestuff (1/10,000) gave very beautiful star-shaped plates (Fig. 5) when treated with 1 drop of phosphotungstic acid. When viewed by polarised light these crystals gave an interesting play of colour. Silicotungstic acid (one drop) also gave characteristic crystals (Fig. 6)—cigar-shaped needles with small nodules near the centre. (These marks are much more pronounced than the photomicrograph would appear to indicate.) These precipitates are two different crystalline forms of free hexanitrodiphenylamine.

VICTORIA YELLOW.—Five drops of dye solution (1/10,000) were treated with 2 drops of concentrated hydrochloric acid and 1 drop of Wijs solution, and boiled for a few seconds, and a piece of granulated zinc immediately added. On standing (12 to 48 hours) a delicate pink colour developed.*

AURINE.—Since the extract from the foodstuff is ammoniacal, this dye will be present as the red ammonium compound. A few drops (0·2 c.c.) of this solution were treated with 2 drops of chrome alum solution, and the lake formed extracted with a little ether. Some of the ether (which is coloured yellow) was extracted with a small pipette and spotted on a microscope slide, when the presence of aurine was indicated by a pink circle appearing on evaporation. This last reaction is given by several lake-forming dyes, but, taken in conjunction with the colour changes of aurine (yellow in acid, red in ammonia), the test becomes distinctive.

The procedure we recommend for the identification of the prohibited dyestuffs is as follows:

The extract of colouring matter (say about 1·5 c.c.) is placed in five small test tubes (0·5 cm. × 6·0 cm.). The contents of the first tube are used for the preliminary test to determine whether the dyestuff is sulphonated or not, as described above. One drop of berberine sulphate is added to the second tube; a precipitate may indicate either picric acid or Martius yellow; the latter can be confirmed by the gold chloride test. If there is no precipitate and no change of colour on adding berberine sulphate solution, the contents of this tube should be tested for Victoria yellow by the reduction test previously mentioned. To the third tube a drop of phosphotungstic acid is added; a precipitate, with decolorisation, may indicate aurantia, which can be confirmed by the reaction with silicotungstic acid. The fourth test tube is used to test for aurine, whilst the fifth tube can be utilised to confirm any of the previous results. It is advisable to allow the precipitates, which are very small, to stand overnight before examining them microscopically. In certain cases it has been possible to identify mixtures of dyes in dilute solution by utilising the methods given above.

Several of the basic dyestuffs give precipitates with the prohibited colours at a dilution of 1 in 10,000, the majority of these precipitates being amorphous.

* It was found that dinitro-para-cresol gave a more intense pink coloration than dinitro-ortho-cresol. The intensity of the pink colour obtained from the Victoria yellow depends on the amount of the para isomer present.

Many of the yellow dyes used in foodstuffs do not dye cellulose acetate (*e.g.* "Celanese"), but it is interesting to note that all the prohibited dyestuffs dye this material yellow to orange shades.

One of us (A. R. J.) is indebted to Mr. T. Cockburn, F.I.C., for much valuable advice, and to Mr. F. W. Harris, F.I.C., for permission to publish this paper.

CITY ANALYST'S DEPARTMENT,
CORPORATION OF GLASGOW.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW.

The Determination of Vanadium in Steel.*

BY A. T. ETHERIDGE. Ph.D., F.I.C.

(*Read at the Meeting, March* 4, 1928.)

METHODS used for this determination have been described and criticised by Cain (Reprint No. 161, *Bulletin of Bureau of Standards*). The author of this paper has already endeavoured to improve the ordinary volumetric method (ANALYST, **1923, 48**, 588). It was pointed out that the process is somewhat limited in its scope, and it is clear that a more accurate method is necessary.

The process described in this paper has been in use for the last three years, and been proved to be accurate for all kinds of steel.

Briefly, the method consists in removing iron and other interfering metals, leaving a solution of the vanadium which can be determined by the ordinary permanganate titration. This is carried out in two main operations, *viz.* removal of iron as chloride by the ether extraction process, followed by removal of the rest of the interfering metals by electrolysis over a mercury cathode. There are no large precipitates to deal with as in Cain's proposed method (*vide supra*), in which excess of cadmium carbonate is used to precipitate the vanadium from a ferrous sulphate solution. Chromium is also precipitated, which is a disadvantage with high chromium steels. The author has adopted Cain's electrolytic purification of the solution, modifying it in detail; in particular, the special apparatus used by Cain has been discarded for an ordinary wide beaker of 800 c.c. to 1000 c.c. capacity, containing a layer of half an inch of mercury. The connection with the current is made by a platinum wire enclosed in a thin glass tube, sealed at the bottom, with a small length of platinum projecting into the mercury. The beaker is covered by a notched glass.

* Communication from the Research Department, Royal Arsenal, Woolwich.

There is nothing new in either of these two main operations, but the combination of them as a means of determining vanadium has not been published, so far as the author is aware. The details of the method, as used for an ordinary nickel-chromium-vanadium steel, are as follows:

PREPARATION OF THE SOLUTION.—The steel, in the form of drillings (5 grms.), is dissolved in 80 c.c. of strong hydrochloric acid in a tall 800 c.c. beaker, oxidised with a few c.c. of nitric acid, digested to complete disappearance of black carbide, evaporated to about 15 c.c., cooled and transferred to a large separating funnel, with the minimum quantity of 50 per cent. hydrochloric acid (equal volumes of strong acid and water) from a wash bottle. Two solutions of ether and hydrochloric acid are necessary; *viz.* solution A, which consists of 50 c.c. of strong acid with 75 c.c. of ether added slowly while cooling; solution B, which consists of 100 c.c. of 50 per cent. hydrochloric acid with 30 c.c. of ether. According to Rothe's directions for removing ferric chloride by ether from a solution in 50 per cent. hydrochloric acid, it is necessary to add 6 c.c. of solution A per grm. of dissolved iron, or 30 c.c. for 5 grms. This is shaken together and cooled. Ether is added till the funnel is about four-fifths full (about 300 c.c.). The contents are then shaken together, cautiously at first, and with frequent loosening of the stopper to ease the pressure due to ether vapour. Finally, it is vigorously shaken and allowed to stand till a clear separation into two layers has occurred. The lower layer is run out into the original beaker. The ether is washed five or six times with 20 c.c. of solution B, together with a few c.c. of hydrogen peroxide (as recommended by Bauer and Deiss, *Sampling and Analysis of Iron and Steel*). Evaporation with hydrochloric acid converts vanadium from the pentavalent into the tetravalent state, in which condition Bauer and Deiss state that its chloride is very slightly soluble in ether. Hydrogen peroxide oxidises it back to the pentavalent state, in which it is insoluble in ether. Each aqueous layer, as it forms after shaking with solution B, is run out into the beaker; besides the vanadium, this liquid contains nickel, chromium, manganese, etc.; also some iron which is not entirely removed by the process; in fact, all the alloy metals present in the steel except molybdenum, which is retained in the ethereal ferric chloride. It is boiled down to a low bulk after removing the excess of ether on a water bath. A little nitric acid is added to oxidise any organic matter derived from the ether, followed by 25 per cent. sulphuric acid, and then the liquid is evaporated slowly at a low temperature until fumes appear. The amount of acid used depends on the amount of metals present; 20 c.c. are sufficient for the ordinary type of vanadium steel under consideration. The "fuming" must be done at the lowest possible temperature, as otherwise it is difficult to dissolve the anhydrous sulphates, particularly chromium sulphate. It is necessary to eliminate hydrochloric and nitric acids before the next operation, but this can be quite well done at a low temperature, if sufficient time is allowed. After cooling, the sulphates are dissolved in 100 c.c. water, which is heated till a clear solution is obtained. The liquid is passed through a small filter to remove silica, neutralised with 50 per cent.

ammonia (equal volumes of strong ammonia, sp. gr. 0·880, and water), and made acid with 15 drops of 25 per cent. sulphuric acid.

SEPARATION OF INTERFERING METALS.—It is now ready for the operation of purification from interfering metals. The liquid is transferred to the electrolytic beaker, 1 grm. of hydrazine sulphate added, and electrolysis carried out at 4 ampères, the anode being a rotating platinum gauze cylinder, such as is used as cathode for copper estimations. The beaker is kept covered, as already stated. Hydrazine sulphate serves to reduce ferric to ferrous iron, and chromic acid (formed at the anode) to chromium salt, and so hastens deposition by saving current which would otherwise be expended on this at the cathode region. As a matter of fact, hydrazine sulphate is essential when chromium is present. In its absence there is formed chromic acid at the anode, followed by a black precipitate (this has not been investigated), which not only obscures the liquid and prevents the removal of chromium from being followed visually, but also hinders the removal of chromium. Iron and nickel (or cobalt) are quickly removed in the amounts usually dealt with. Manganese may go into the mercury to some extent (?), but chiefly gathers on the anode. It is quickly removed when more hydrazine sulphate is added. Manganese is immaterial, since it has no influence in the subsequent procedure.

Chromium is the most difficult metal to remove. It has been found that 0·75 grm. is the largest amount that can be conveniently removed in one day (= 15 per cent. of chromium).

During the electrolysis it is necessary to neutralise with 50 per cent. ammonia the free acid formed from time to time. The liquid must not be allowed to become ammoniacal for any appreciable time. The formation of a discoloration indicates too much ammonia, which is immediately neutralised, by a few drops of 25 per cent. sulphuric acid. Electrolysis is continued for 6 hours, after which the liquid is drawn off through a siphon into a large beaker. When the level of liquid has fallen nearly to the end of the siphon tube, about 200 c.c. of hot 5 per cent. ammonium sulphate, slightly acidified with sulphuric acid, are added carefully so that no mercury is thrown up into the siphon. The liquid is allowed to run out as before, and the washing process repeated four times. The current is kept on during the washing and is constant at 4 ampères by the use of ammonium sulphate solution instead of water. Formation of ammonium amalgam is avoided by having the solution hot and slightly acid.

TITRATION OF THE VANADIUM.—The liquid is filtered into another large beaker to remove the small amount of flocculent mercury which usually accompanies it. It is then boiled down to about 200 c.c., the acidity increased by adding about 20 c.c. of 25 per cent. sulphuric acid, cooled somewhat, and saturated with hydrogen sulphide gas. This removes traces of soluble mercury (also arsenic if present), which quickly coagulates and is filtered off, the filtrate being collected in a large flask. After boiling off the hydrogen sulphide gas, excess of a saturated solution of potassium permanganate is added to the boiling liquid from a dropping bottle until a permanent precipitate of manganese dioxide results. The liquid is cooled somewhat, and after addition of an excess of sulphur dioxide saturated solution,

is boiled vigorously for half-an-hour, cooled to 70° C., and titrated with $N/10$ permanganate solution

1 c.c. $N/10$ permanganate = 0·0051 grm. of vanadium.
= 0·102 per cent. on 5 grms. of steel.

Therefore one drop = 0·005 per cent. on 5 grms. of steel.

Experience has shown that this titration is accurate to at least one drop, so that the error from this source is less than 0·01 per cent.

The following table shows results obtained with vanadium percentages from 0·10 to 1·00, by the use of electrolytic iron and standardised ammonium vanadate solution, of which 1 c.c. = 0·001 grm. of vanadium. The ammonium vanadate solution was standardised by the permanganate titration, as previously described. Five grms. of electrolytic iron were used in all cases.

TABLE I.

Vanadium, added, per cent.	0·10	0·20	0·30	0·40	0·50	0·60	0·70
	0·80	0·90	1·00				
Vanadium, found, per cent.	0·10	0·20	0·31	0·40	0·495	0·61	0·70
	0·805	0·895	1·01				

The following table gives results with nickel and chromium added:

TABLE II.

Vanadium added. Per Cent.		Vanadium found. Per Cent.
0·10	Nickel 3. Chromium 1.	0·10
0·20		0·20
0·30		0·30
0·75		0·74
0·25	Nickel 5. Chromium 5.	0·26
0·50		0·50
0·75		0·76

British Chemical Standard V steel. 0·30 repeatedly.
= Nickel nil. Chromium 0·86.

It is necessary to consider some special steels.

SPECIAL STEELS: (1) *High Silicon Steels.*—Silicon may be present up to 2 per cent. After dissolving as usual and evaporating, water is added, silica filtered off, burnt, and heated to fuming with hydrofluoric and sulphuric acids, burnt again, and the residue dissolved in hydrochloric acid and added to the main solution, which is again evaporated. The rest of the procedure is the same as usual. Vanadium is not co-precipitated with silica, but, as the latter is gelatinous and difficult to wash, it is safer to carry out the process described above.

(2) *Tungsten Steels.*—Hydrochloric acid throws out tungsten as a black residue. According to the nature of the steel and its heat treatment, the tungsten is accompanied by vanadium, phosphorus, iron, nickel, etc. On oxidising and digesting for some time, tungstic oxide is formed, and vanadium, etc., are occluded.

Evaporation is continued till a pasty condition is reached; this is followed by treatment with hot 5 per cent. hydrochloric acid and filtration. The filtrate is evaporated and treated as described for the usual procedure.

Recovery of Vanadium from Tungstic Oxide.—The simplest method is that given by S. G. Clarke (ANALYST, **1927, 52, 466**), in which the vanadium is precipitated with cupferron. Prior to this a more laborious but quite accurate method was used which need not be given here. The cupferron precipitate is burnt at a low temperature to vanadium pentoxide, and dissolved in the sulphuric acid used in the sulphating process prior to electrolysis. It cannot be held over till the end, because it contains traces of iron, etc., derived from the impure tungstic oxide.

It is important that tungstic oxide should be completely removed from the steel, as described. It has a tendency to become colloidal, which is overcome during evaporation. If it is not all removed at this stage, it will gradually precipitate later on, and it has been found that suspended tungstic oxide prevents complete removal of chromium by electrolysis (probably by lowering the overvoltage at the mercury surface; suspended pulp in a fine state of division has the same effect).

In considering the cause of occlusion of vanadium, etc., by tungstic oxide, it follows that these effects could not be imitated by adding tungstic oxide to electrolytic iron; consequently no tests could be made in this way. British Chemical Standard Steel W (16·2 tungsten, 3·01 chromium, 4·76 cobalt, 0·44 nickel) has given, on repeated testing, a vanadium content of 0·775 to 0·780 per cent.

(3) *High Chromium Steels.*—Up to the present time vanadium has not been found in these steels (stainless steels). Therefore, it is better to make a qualitative test first. Owing to the intense green colour of these steels when dissolved, it is impossible to carry out the hydrogen peroxide test directly, as can be easily done in other steels. The chromium must be removed. This is done by dissolving 1 grm. in hydrochloric acid, oxidising with nitric acid, and then adding 30 c.c. of 25 per cent. sulphuric acid and evaporating to fumes at a low temperature. After cooling, dissolving in hot water (digesting till clear) and filtering from silica, the free acid is neutralised, 15 drops of 25 per cent. sulphuric acid are added, and the liquid is electrolysed over mercury, as described. After a few hours the metals are deposited in the mercury, as shown by the disappearance of colour; the electrolyte is then drawn off without washing, concentrated by boiling and tested with hydrogen peroxide, care being taken to observe the acidity, conditions, etc., as laid down by Meyer and Pawletta (*Z. anal. Chem.*, **69**, 19).

It has been mentioned before that not more than 0·75 grm. of chromium can be conveniently removed in one day by electrolysis. Should vanadium be found and the chromium be greater than 15 per cent., there are several ways of overcoming the difficulty:

(*a*) Less than 5 grms. of steel can be taken, to bring down the amount of chromium to 0·75 grm. This reduces the accuracy somewhat, as compared with the ordinary procedure of working on 5 grms.

(*b*) The solution for electrolysis can be divided into two (or more) parts, electrolysed separately, and subsequently re-united. This is the best plan if there is apparatus to spare.

(*c*) Cupferron can be used to precipitate vanadium after the ether extraction process. It has the advantage that chromium is not precipitated, but iron (and copper if present) is precipitated as well. It is therefore necessary to make a double ether extraction. The aqueous extract from the first ether treatment is returned to the separating funnel, and the process repeated with fresh ether. Washing with solution B is carried out as before. This reduces the iron considerably. The ether is evaporated off, the acidity reduced to about 5 per cent., and 3 grms. of cupferron dissolved in water are added. After standing a short time the precipitate is filtered off. As it is bulky and plastic, it is not easy to wash it free from chromium, etc. It is best washed by decantation first, the precipitate being pressed with a glass rod to squeeze out most of the liquid. It is not necessary to wash it exhaustively, as it must be purified from iron in the subsequent work, during which chromium, etc., are also separated. The precipitate is burnt at a low temperature, dissolved in 20 c.c. of 25 per cent. sulphuric acid, the acidity adjusted, and electrolysis carried out as described. It is important to burn off at a low temperature, as otherwise chromium oxide does not dissolve readily. The rest of the procedure is as usual. Tests made on electrolytic iron with varying amounts of vanadium from 0·10 to 1·00 per cent., and also containing 20 per cent. of chromium, have given vanadium figures correct to within 0·01 per cent.

The results given by method (*a*) are not quite so good, but are correct to 0·02 per cent. with steel containing 1·00 per cent. of vanadium, and better than this with 0·10 to 0·50 of vanadium. With method (*b*) the figures are also correct to within 0·01 per cent.

Molybdenum Steels.—As already mentioned, molybdenum is removed in the ether and ferric chloride. Any small amount carried forward in the aqueous extract is removed over mercury by electrolysis.

High Manganese Steels.—During electrolysis large amounts of manganese dioxide are formed, partly on the anode and partly suspended in the liquid. Hydrazine sulphate suppresses it, so that the course of the deposition can be followed visually at any moment. Apparently manganese does not enter the mercury to any extent, but this is of no consequence, as (like aluminium) it has no influence on the final permanganate titration.

The Use of Mitchell's Ferrous Tartrate Reagent in Studying the Precipitation of Alkaloids by Tannin.

By ARTHUR EDWARD JONES, B.Sc., A.I.C.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, May 2, 1928.)

A colorimetric method of determining gallotannin was devised by Mitchell (Analyst, **1923**, **48**, 2), and its accuracy was confirmed by Nicholson and Rhind (Analyst, **1924**, **49**, 505), and by Glasstone (Analyst, **1925**, **50**, 49). The primary aim of the present investigation was to ascertain whether it is possible to apply this method to the indirect determination of alkaloids. In other words, is it possible to precipitate a given alkaloid by adding a measured excess of gallotannin, and, by determining colorimetrically this excess in the filtrate from the alkaloid tannate, to calculate the amount of alkaloid in the precipitate?

The gallotannin used in the experiments was some of the original material used by Mitchell in establishing his method. This contains 1·2 per cent. of moisture, 10·5 per cent. of gallic acid, and less than 1 per cent. of glucose. Nierenstein (Analyst, **1923**, **48**, 321) confirmed the fact that this tannin is practically free from glucose, finding it to contain only 0·6 per cent. by polarimetric determination, and 1·6 per cent. by a reduction method.

As this gallotannin was used both for the precipitation of the alkaloid and as the colorimetric standard for the determination of the excess of tannin in the filtrate, the gallic acid and moisture present were constants throughout the process, and so did not affect the calculation of the amount of gallotannin taken up by the alkaloid.

Experiments with Quinine.—As quinine hydrochloride is used for separating gallotannin from gallic acid in Mitchell's method (*loc. cit.*), experiments were first made to study the action of the reverse process, *viz.* the precipitation of the alkaloid by excess of gallotannin. When dilute solutions were mixed in this order it was found that the precipitated tannate was colloidal in form, and could not be separated either by filtration or centrifugal force without the addition of a coagulating agent, such as sodium chloride. As the addition of salt affected the colour obtained with Mitchell's ferrous tartrate reagent, it was necessary to add the same amount of salt to the standard solution.

An attempt was made to use kieselguhr as a coagulant, but it was found that it adsorbed tannin from the solution. In one experiment 1 grm. of kieselguhr adsorbed 0·26 grm. of gallotannin (allowance being made for the gallic acid and moisture present).

As the solution after treatment with quinine hydrochloride had a P_H value of less than 8·5, the hydrogen ion concentration required readjusting to obtain the maximum intensity of coloration with the ferrous tartrate reagent (*cf.* Glasstone, *loc. cit.*).

ADSORPTION OF TANNIN BY QUININE TANNATE.—Quinine tannate was prepared by adding an aqueous solution of quinine hydrochloride to an excess of a solution of gallotannin. The precipitate was coagulated by adding salt, and filtered off on a Buchner funnel. It was not found possible to wash the precipitate free from sodium chloride, since complete removal of the salt caused a colloidal solution of the alkaloid tannate to be formed. On shaking a small quantity of this tannate with 50 c.c. of a 0·1 per cent. solution of gallotannin, and determining the residual tannin colorimetrically, it was found that 40 per cent. of the 0·5 grm. of tannin present was removed from the solution.

The extent of the adsorption of tannin by quinine tannate was found to depend upon the amount of gallotannin present when the alkaloid tannate was formed. Thus, a tannate prepared in a solution containing a slight excess of tannin would have a different composition from one prepared in the presence of a large excess, and both would be very different from the precipitate formed in a solution containing an excess of alkaloid.

EXPERIMENTS ON CHANGE OF CONCENTRATION.—A series of determinations was made in which the amounts of 1 per cent. gallotannin solution and of 10 per cent. sodium chloride solution were kept constant, whilst the amount of quinine hydrochloride was varied. The following results were obtained:

Gallotannin sol. (1 per cent.)	Sodium chloride sol.	Quinine hydrochloride sol.	Concentration of gallotannin in sol.	Amt. of tannin taken up by quinine.
c.c.	c.c.	c.c.	Per Cent.	Grm.
50	1	10	82	0·104
50	1	20	70	0·227
50	1	30	62	0·354

Obviously, the amount of adsorption of gallotannin shows some roughly approximate relationship to the amount of quinine tannate present, but does not afford an accurate measurement of the amount of quinine present; otherwise the figures would have been 0·104, 0·208 and 0·312 grm.

AMOUNT OF SODIUM CHLORIDE REQUIRED FOR COAGULATION.—As it was found that a further deposit of alkaloid tannate separated from the clear filtrates from the precipitates thus formed, experiments were made to determine the minimum amount of sodium chloride required to effect the separation of the whole of the tannate. A mixture of 100 c.c. of 1 per cent. gallotannin solution, 10 c.c. of 0·1 per cent. quinine hydrochloride solution, and 2 c.c. of 10 per cent. sodium chloride solution was filtered, and the bright filtrate was evaporated to dryness. The residue was then tested for nitrogen by heating it with metallic sodium, treating the product with water, and testing the solution with ferrous sulphate, followed by hydrochloric acid until the precipitate just redissolved, and finally

adding one drop of ferric chloride solution. A strong Prussian blue reaction was obtained.

With 100 c.c. of 1 per cent. gallotannin solution, 10 c.c. of 0·1 per cent. quinine hydrochloride solution, and 5 c.c. of 10 per cent. sodium chloride, the reaction was still pronounced. But by increasing the amount of salt solution to 10 c.c. only a very faint Prussian blue reaction was obtained. Hence, 10 c.c. of 10 per cent. sodium chloride were added as coagulant in the subsequent work.

COMPARATIVE RESULTS WITH QUININE HYDROCHLORIDE.—The following results were obtained by adding the quinine solution and salt solution to the gallotannin solution, filtering off the precipitate after 30 minutes, and determining the excess of gallotannin in the filtrate.

Gallotannin solution (1 per cent.).	Quinine hydrochloride solution (0·1 per cent.).	Sodium chloride solution (10 per cent.).	Tannin taken up by quinine.
c.c.	c.c.	c.c.	Grm.
50	10	10	0·234
50	20	10	0·332
50	5	10	0·180
50	10	20	0·228
50	20	10	0·344
50	20	10	0·324

In a second series of experiments the results were as follows:

Gallotannin solution (1 per cent.).	Quinine hydrochloride solution (0·1 per cent.).	Sodium chloride solution (10 per cent.).	Tannin taken up by quinine.
c.c.	c.c.	c.c.	Grm.
100	10	10	0·352
50	10	10	0·311
50	10	10	0·311

These results also show that the amount of adsorption depends upon the quantity of gallotannin present.

EXPERIMENTS WITH CINCHONINE.—It has been shown by Chapman (ANALYST, 1908, **33**, 372; 1909, **34**, 372), and confirmed by Hooper (ANALYST, 1925, **50**, 162) that the tannate obtained by treating gallotannin with excess of cinchonine sulphate contains 4·3 per cent. of nitrogen, corresponding to a proportion of 55 per cent. of tannin in the cinchonine tannate. The compound formed between hop tannin and cinchonine contains the same amount of nitrogen (Chapman, *loc. cit.*), as does also the cinchonine tannate made from tea tannin (4·32 per cent., Smith, ANALYST, 1913, **38**, 312), and in cacao tannin (Jensen, ANALYST, 1928, 368). Cinchonine tannate from these sources thus contains approximately 55 per cent. of tannin, and in the series of results given in the following table the amount of tannin corresponding to the cinchonine taken has been calculated by the use of the factor 1·2. The difference between this calculated combined tannin and the

total amount removed from the solution gives the amount of tannin adsorbed by the cinchonine tannate.

Gallotannin solution (1 per cent.). c.c.	Salt solution (10 per cent.). c.c.	Cinchonine solution (0·1 per cent.). c.c.	(a) Gallotannin removed. Grm.	(b) Combined tannin (cinchonine × 1·2). Grm.	Difference (a–b) = tannin adsorbed. Grm.
50	10	10	0·122	0·012	0·110
100	20	10	0·103	0·012	0·091
50	10	30	0·374	0·036	0·338
50	10	30	0·356	0·036	0·320

From these results it will be seen that the cinchonine tannate had adsorbed from 4·2 to 5·1 (average 4·8) times its weight of gallotannin. As it does not seem possible to prevent or to standardise this adsorption (mainly owing to the difficulty of determining the exact amount of salt required), an indirect colorimetric method of determining alkaloids is not practicable, although, as has been shown, the colorimetric method affords a means of measuring the adsorption of gallotannin by alkaloid tannates.

My thanks are due to Dr. Nierenstein for the interest he has shown in the work and the advice he has given.

BIO-CHEMICAL LABORATORY,
THE UNIVERSITY, BRISTOL.

Coffee Parchment as an Adulterant of Bran and Sharps.

BY JOHN EVANS, F.I.C., AND T. E. WALLIS, B.Sc., F.I.C.

(*Read at the Meeting, April* 4, 1928.)

THE use of this substance as an adulterant of bran and sharps first came to the notice of the writers in the year 1924.

Enquiry elicited the fact that in 1902 an article described as parchment coffee husk was reported to the Ministry of Agriculture as having been imported for use in adulterating bran and bean meal.*

In 1904 a sample of bran was reported as containing about one-third of coffee husks. Recently a further case has come to our knowledge, and, in view of the recrudescence of this practice, we feel that the present note may be of use to agricultural chemists.

In bran, where the particles of parchment are fairly large, they may be recognised by their pale buff colour, resembling old ivory, and their perfectly homogeneous, semi-opaque appearance, both surfaces being similar. They are quite free from adhering starchy matter, show no definite lines, ridges or striations,

* Coffee parchment should not be confused with the seed-coat, the remains of which are found in the groove of the coffee berries of commerce.

and are stiff, hard, shiny and usually slightly curved. In sharps the parchment is usually much more finely comminuted. A few of the suspected pieces should

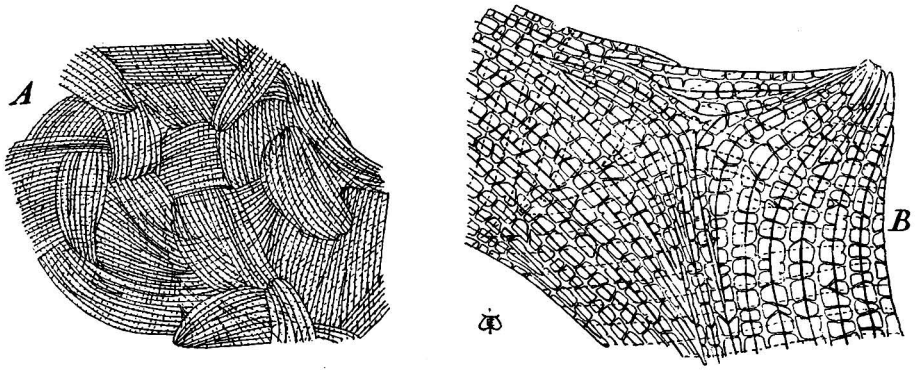

FIG. 1. Coffee parchment (endocarp) seen in surface view.
A. A portion of the endocarp drawn semi-diagrammatically (× 50).
B. A small piece of the same, showing details (× 200).

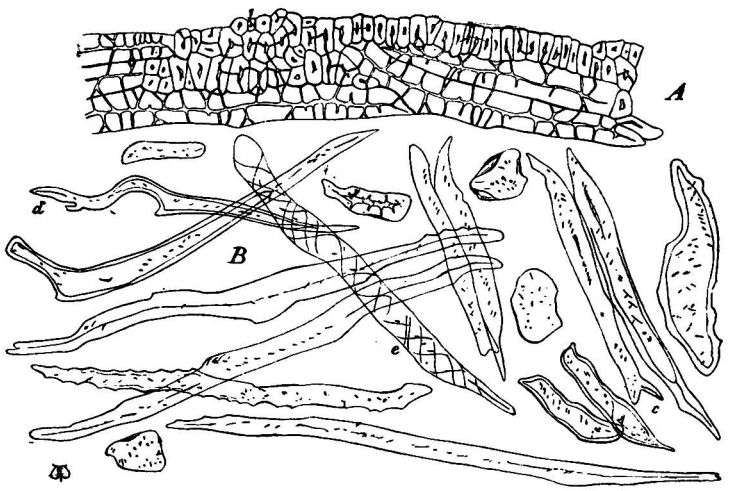

FIG. 2. Coffee parchment (endocarp).
A. Transverse section (× 200).
B. Cells of the endocarp isolated by maceration in potassium chlorate and nitric acid.
c & d. Ends of cells showing a forked formation.
e. A cell showing spiral marks due to pressure upon the cover glass (× 200).

be boiled with chloral hydrate solution (chloral hydrate 5, water 2) till rendered transparent, and a piece mounted in chloral hydrate for microscopical examination.

When the parchment is present in starchy material like sharps to a small extent only, it is advisable to prepare a crude fibre, which is done most expeditiously by the Dutch process (see Wallis, *Analytical Microscopy*, p. 66), which can then be examined microscopically.

The amount of parchment present in a sample can be calculated from the crude fibre, coffee parchment yielding about 60 per cent., and bran and sharps about 10 per cent.

Coffee parchment consists of the thin and tough endocarp of the coffee fruit. A transverse section (Fig. 2.A) shows it to consist of three or four layers of lignified, thick-walled sclerenchyma. The cells of any one layer frequently cross those of other layers at right angles or nearly so. Each separate layer consists of groups of cells whose long axes are parallel to one another, and the various groups are orientated in different directions, so that, in surface preparations viewed under a low magnification, the tissue appears to be divided up into irregular square or rectangular areas, each consisting of a collection of elongated cells arranged with their long axes parallel (see Figs. 1.A and 1.B).

The individual cells of the endocarp, isolated by maceration in a solution of potassium chlorate and nitric acid, are seen to have the forms shown in Fig. 2.B. If, in mounting a maceration preparation, pressure is used to aid the separation of the cells, many of them show the spiral lines represented upon one of the cells, *e*, in Fig. 2.B. The cells vary in length from 125μ to 650μ, with a most frequent length of about 425μ; in height (radial measurement) they vary from 17·5μ to 45μ, the most frequent values being from 25μ to 30μ, and in width (tangential measurement) 12μ to 30μ, a common size being 17μ. The two transverse measurements refer to the middle region of the cells which generally taper towards their ends. These ends are sometimes irregularly forked (Fig. 2.B., *c* and *d*), or are strongly serrated. The margins of the cells are often coarsely toothed where they abut upon a series of adjacent cells, crossing them at right angles; the lumen is quite small and the very much thickened and lignified walls are perforated by numerous simple pits. Occasional cells are markedly shorter than the majority (down to 50μ), though of equal or even greater width.

Discussion.

Mr. G. D. Elsdon wrote as follows:

Through the kindness of Mr. John Evans I have been able to see an advance copy of the interesting paper by Evans and Wallis. Some few months ago a sample of bran was submitted to me which was found to contain fibre 24·6 per cent., albuminoids 10·95 per cent., ash 4·6 per cent., and from which some 25 per cent. of fairly large, hard, yellowish fragments could be picked out. Microscopical examination of these showed them to consist of coffee parchment.

My colleague, Mr. J. R. Stubbs, removed the parchment from whole coffee berries, and found it to have the following characters:—Ash, 3·3 per cent.; ether extract, 2·5 per cent.; fibre, 51·5 per cent.; and albuminoids, 5·25 per cent.

A sample of "Thirds" received at the same time and from the same source was found to contain 16·8 per cent. of fibre, and 3·3 per cent. of ash, but in this case the microscopical characters were those of wheat fibre, and no material foreign to wheat was detected.

Dr. J. A. Voelcker mentioned that this was a recrudescence of an old practice to which he had drawn attention in his annual Reports to the Royal Agricultural Society of England, and he exhibited specimens, taken as far back as 1904 and 1905, in which there had been adulteration of both bran and sharps with coffee parchment. He had little doubt that adulteration took place in this country, as he had had samples submitted to him by millers who wished to know whether it was a suitable food for stock.

Note.

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

THE PRECIPITIN TEST FOR BLOOD.

My comments on Mr. Shrewsbury's note (ANALYST, 1928, 380) are as follows:—I have no experience of guinea pigs, but they are generally stated to be unsatisfactory for this work, and, in addition, yield very much less blood than a rabbit. The fowl I use but little, as, although one gets high titre, the serum is often non-specific and, as a result, becomes dangerous to use without very adequate controls. Questions of dosage are very difficult, and nearly every worker has his own pet dosage. In my experience Lloyds' dosage has given poor results. Purchased sera all have one great drawback—their history; such factors as temperature during transit, amount of agitation they have received in the post, age, and other unknown influences render them, in my opinion, undesirable. It is essential that the worker should make his own serum, and I make it a rule not to supply my sera to anyone, and I know of other workers who adopt the same attitude.

In the tropics many workers find that sera cannot be kept more than three months, but in this country one is often able to keep them longer. I offer no explanation for this or any of the other changes which sera may undergo. I quite agree with Mr. Shrewsbury's remarks on the P_H value. With regard to the application of the test—I prefer the layering, but the technique is not so easy to do as the rolling-down method described. This is, of course, a matter of opinion.

G. ROCHE LYNCH.

DEPARTMENT OF CHEMICAL PATHOLOGY,
ST. MARY'S HOSPITAL, PADDINGTON, W.2.

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.

LEAD IN TARTARIC ACID. PRICE LIST AS WARRANTY.

THE Glasgow Stipendiary Magistrate recently delivered judgment in a case of the Health Authority against a Glasgow druggist for the sale of tartaric acid containing 48 parts of lead per million, being 28 parts in excess of the B.P. limit.*

The defence was that the tartaric acid was purchased with a warranty, and, with reference to this plea, it is pointed out in the judgment that the question of warranty is still in a very unsatisfactory state. In the case of *Jeynes* v. *Hindle* (1921, 2K.B., 581), decided in the English Courts, there was an oral contract for

* Abridged report from *Pharm. J.*, 1928, **120**, 359.

the sale of quinine wine to be made according to the British Pharmacopoeia, and each bottle bore a label to that effect. The wine had not been made according to the British Pharmacopoeia, and the seller was prosecuted. The judges held that as a warranty was neither contained in the contract of sale nor given afterwards, in pursuance of a stipulation in the contract of sale, it afforded no defence.

In the Scottish case of *Chalmers* v. *Morton* (1922, J.C., 65), which was carried on appeal to the High Court of Justiciary, it was argued that the warranty only stated that the milk was pure as it was milked from the cows, and not that it was pure at the time of sale by the retailer. It was held that the warranty should be construed as applying to the condition of the milk at the time of delivery to the defendant. The judges thought that the warranty should be in the contract, but they held that the contract was constituted by a course of dealings over a considerable period of time, and that, as the invoice contained a written warranty, it was part of the contract.

About the same time a decision was given in the English King's Bench Division in the case of *Dewey* v. *Faulkner* (1922, 29 T.L.R., 130) to the effect that a warranty on the label was not sufficient.

In the present case, continued the Stipendiary, the question was whether there was a sufficient warranty in law. He felt bound to follow the decisions of the Scottish Courts, in spite of the fact that they were apt to create an undesirable looseness in practice. In this case the defendant had received the tartaric acid from a wholesale firm, who, according to the defence, had a warranty from the manufacturers, and who, in turn, warranted the acid to the defendant. The warranty was contained in the price list of drugs issued by the wholesale firm, and the connecting link between that warranty and the tartaric acid in question was supplied by the course of dealing between the parties. There was an implied course of dealing, and that would appear to be sufficient to validate the warranty received by the defendant. The case was very thin on this question, but, in view of the dicta of the Scottish judges in *Chalmers* v. *Morton*, he must sustain it and discharge the defendant from the prosecution. At the same time, he would prefer to see some more satisfactory form of warranty adopted for use in cases such as this.

Parliamentary Notes.

RECONSTITUTED AND SYNTHETIC CREAM.

A BILL to control the production, distribution and sale of reconstituted and synthetic cream.*

(*Ordered to be brought in by Mr. Everard, Colonel Acland Troyte, General Clifton Brown, Dr. Davies, Captain Robert Henderson, Mr. Lamb, Mr. Riley, Mr. Smith-Carington, and Mr. Alfred Williams.*)

The Bill was ordered, by the House of Commons, to be printed, May 8, 1928.

* [Bill 125]. H.M. Stationery Office. Price 2d. net.

The Chemistry of Wine Making.

A REPORT ON OENOLOGICAL RESEARCH.*

THIS report, prepared by Dr. Hewitt for the Empire Marketing Board, deals with all the processes of the fermentation of the fresh juice of grapes by means of wine yeast, and is largely based on a consideration of the methods used in France or French North Africa, which together produce more than half of the wine made in the world.

THE VINE: INFLUENCE OF SOIL AND CLIMATE.—Each variety of grape (cépage) has its own special characteristics (acidity, yield of alcohol, astringency, bouquet), and in some vineyards two or more varieties of grapes are grown in order to obtain complementing qualities. Several examples of the influence of soil on the quality of wine are given. For example, *Pisiol*, when grown in Burgundy on a calcareous soil, yields celebrated wines; whereas, when grown on a compact clay soil, it yields a wine of almost ordinary quality. As a general rule, grapes grown in temperate climates show a greater ratio of acid to sugar than those raised in warmer regions. Whilst the European vine (*Vitis vinifera*), of which there are over 2000 varieties, will accommodate itself to most soils, this is not the case with the various American species. The American vines, however, resist the attack of pests better than the European; hence, French vines are grafted on to American stocks. This is often successful, but the soil is not always suitable.

Much work has been done on the production of hybrids which, while resistant to phylloxera and cryptogamic maladies, yield grapes capable of conversion into reasonably good wine. The earlier hybrids were imported from America; the newer *producteurs directs* are, for the most part, the result of the work of French viticulturists.

THE COMPOSITION OF GRAPES AND MUST.—A full summary of the composition of grapes and the must obtained from them is given, together with references to the original literature. There is also an account, with more detailed information, of various constituents of the must, including sugars, inosite, organic acids, pectins, tannins, colouring matters, fats, nitrogenous compounds, enzymes, and inorganic salts.

YEASTS AND THE FERMENTATION PROCESS.—The conditions for the best results to be obtained are discussed. As wine yeasts prefer an acid medium, it is generally agreed that when musts are deficient in acid the acidity should be increased, either by direct addition of tartaric acid, or by indirect means.

Other factors affecting the yeast are dealt with under the following heads:—(i) The influence of substances, other than sugars, in the must on living yeast; (ii) The by-products of alcoholic fermentation; (iii) The resistance of different races of *Saccharomyces ellipsoideus* to changes of environment, *e.g.* chemical composition of the must, temperature, etc., and variation in the products formed by them.

When the influence of race on the qualities of the resulting wine was first recognised, great hopes were entertained of effecting radical alterations in the value of inferior vintages. Sterilisation of must, followed by fermentation with yeast from a celebrated vinery, was expected to give a wine approximating in character to that produced by the yeast in its native habitat. These expectations

* By J. T. HEWITT, D.Sc., F.R.S. Pp. 57. H.M. Stationery Office. 1928. Price 1s. net.

were only realised to a very limited extent, for part of the bouquet of wines is contributed by substances originally present in the grape, irrespective of all fermentation; and even these substances vary in quantity, not only with the cépage, but also with the soil on which the cépage is grown and the general climatic conditions.

Whether it is desirable to use an imported race or to select an indigenous yeast is a question on which there is some difference of opinion. If grapes are being introduced into a new neighbourhood, it is probably wiser to import a cultured yeast, as there is a possibility that the local races of wild yeast may be unsuitable for wine making.

STANDARD PROCESSES OF MANUFACTURE.—The various types of machinery used in the manufacture of red and white wines are described. The use of ferro-concrete fermenting tanks of a greater capacity than 12,000 gallons has not proved very successful. The chief difference between manufacturing red and white wines lies in the fact that in the latter case the must is not fermented in contact with the stalks or the skins. Since the cells of the skins contain matters contributing to the bouquet and these are not extracted, as in the case of red wine, during the first strong fermentation, it is necessary to leave the vintage until the maturation of the grapes is complete and even to allow them to become over-ripe. In fact, the practice obtains in some neighbourhoods (*e.g* the Sauternes) of delaying the vintage until the grapes begin to dry and are covered with a mould, *Botrytis cinerea*. The effect is to render the skin permeable to water and also leads to the consumption of acid, with the result that the must of such grapes is very saccharine without being unduly acid.

If it is desired to use as large a proportion of the must as possible for making white wine, the pink must be obtained by uniting the liquids resulting from draining, and the first pressing is decolorised. The following methods are in use:—1, Sulphur dioxide, either as gas or as potassium bisulphite; 2, Decolorising carbon, animal black, &c.; 3, Martinand's process—simultaneous employment of aeration and animal black; 4, Martinand and Semichon's process—aeration and sulphiting.

When sulphur dioxide is alone resorted to, its disappearance by evaporation or combination is accompanied by a reappearance of the colour. This is obviated in Martinand and Semichon's process, in which air is pumped into the must until it begins to turn yellow. At this stage, 6 to 10 grms. of potassium bisulphite are added per hectolitre with a view to preventing the oxydase continuing its action after fermentation.

Vins gris, Vins rosés.—A certain amount of wine is marketed in France under these names. A *vin gris* is a slightly coloured white wine made with red grapes. The must obtained by draining is united with the must from the presses and fermented without previous clarification. *Vins rosés* are generally obtained from red grapes (which may or may not be mixed with one-fifth of white grapes). When the fermentation is well established, and before the colouring matter has been much dissolved, the must is run off rapidly into casks and allowed to finish as in the method of making white wines.

Fortified Wines.—These are put on the market with as much alcohol as 15 to 20 per cent. by volume. They also contain a certain amount of unfermented sugar and are generally obtained by allowing a must to begin to ferment and then adding pure alcohol or wine spirit. A highly saccharine must is taken for making wines of this character; a distinction may be drawn between the case where fully ripe grapes have been taken and where the grapes have been partially dried with a view to increasing the percentage of sugar in the must.

A special case is that of *Mistelles*; these are made by adding 15 or 18 per cent. of alcohol directly to a must before any fermentation has started and mixing well.

IMPROVEMENTS IN MANUFACTURE.—In this section are considered the changes made by (*a*) additions to the must, (*b*) modifications of the fermentation process, and (*c*) mechanical alterations.

(*a*) ADDITIONS TO MUST: *Sugar.*—The addition of sugar to must is generally allowed. On the other hand, if grapes are too rich in sugar, addition of water is forbidden in France and other countries. This generally results in more alcoholic wine being produced in countries where the grape ripens very rapidly; indigenous yeasts are accustomed to very saccharine juice and are usually able to complete the fermentation unless the sugar content is abnormally high. Simultaneous addition of sugar and water ("gallisation") is considered fraudulent in France.

Acid.—Direct addition of tartaric acid to must is generally permitted, although it is rarely required in temperate climates. Simultaneous addition of sugar and tartaric acid is not allowed by French law.

By the Decree of Aug. 10, 1921, Article 3, Dec. 10, the addition of crystallised citric acid in amounts up to, but not exceeding, 0·5 grm. per litre, is allowed in France, with the object of preventing "casse."

The alternative method of increasing the amount of tartaric acid in solution, *viz. plastering* (*platrage*), consists in powdering the grapes, either before or after crushing, with plaster of Paris, which reacts with the potassium hydrogen tartrate present.

Hydrogen calcium phosphate also liberates tartaric acid from hydrogen potassium tartrate, but its use is restricted in France to the amount necessary for the normal development of the yeast.

According to the French decree (Art. 3, Sect. 17), crystallised ammonium phosphate or ammonium glycero-phosphate may also be used for nourishing the yeast.

If wine contains too much tartaric acid the fault is remedied by the addition of neutral potassium tartrate.

Tannin.—The addition of tannin is necessary, and is allowed in France in an amount sufficient to effect clarification by means of albumin, casein, gelatin, etc. Since the amounts of these albuminous substances are not limited, there is no practical limit to the amount of tannin which may be added.

Colour.—The addition of artificial colouring matters is prohibited, but French law permits coloration by means of caramel which has been obtained from concentrated grape must.

Sulphur Dioxide and Sulphites.—French law places no restriction on the amount of pure sulphur dioxide employed, but limits the quantity of pure alkaline bisulphites to a maximum of 20 grms. per hectolitre.

(*b*) MODIFICATIONS OF FERMENTATION PROCESSES.—Preliminary heating of the must is done (*a*) with the object of starting fermentation, (*b*) of sterilising the must, and (*c*) of altering the composition, *e.g.* as regards pectic substances.

The effects of "passerillage" (partial drying of grapes before crushing being effected) on the composition of Grenache must have been noted and compared with the results obtained with concentrated fresh must which had been concentrated

artificially to the same sugar content as that shown by the must of the partly dried grapes.

	Grms. per litre.			Grms. pectose per Kilo. of marc.
	Sugar.	Acidity.	Pectin.	
Natural must (Grenache)	360	3·25	1·54	2·53
Must after 12 days passerillage ..	502	3·30	5·25	3·80
Increase per cent.	34·9	1·54	240·0	50·2
Natural must concentrated artificially	502	4·53	2·67	3·53

Whilst Müntz and Lainé regarded the wine-gum as being produced from the pectic compounds, Semichon and Flanzy consider it to be a product of yeast metabolism and state that it yields glucose on hydrolysis.

Certain deductions can be drawn from these results:—

1. The content of pectin allows one to draw a distinction between sweet alcoholic wines made from super-matured grapes and those made from an artificially concentrated must. The gums allow of a distinction between the former and "mistelles."

2. The amount of pectin varies with the variety of grape. Grapes which are suitable for "passerillage" (*e.g.* muscat, grenache, malvoisie) give musts rich in pectin and wines which are "moelleux." The contrary holds for clairette, picpoul, aspiran.

3. A wine with velouté may be obtained instead of a dry wine by warming the fresh marc with a part of the must, when the acid transforms the "pectose" into soluble pectin.

4. The results explain the methods employed by the Greeks and Carthaginians for obtaining "vins veloutés et parfumés."

5. There is a relationship between "le moelleux" and the bouquet of fruits. The latter appears to be formed by the dissociation of the methyl pectate, owing to the action of the methyl radical on the essences and oleoresins contained in the grape.

Cooling Fermenting Musts.—Whilst in cool countries it may be necessary to warm the must to 20° to 25° C. to start fermentation, cooling may be necessary in a warm country. In Algeria the use of cooling appliances (described in the report) is common.

Control of temperature may also be effected by reducing the speed of fermentation by addition of sulphur dioxide, both for white wines and red wines.

Sterilisation and Muting of Musts.—The sterilisation of a portion of the must is required if selected yeasts are employed. This may be effected by heating and subsequent cooling or by addition of a large amount of sulphur dioxide and subsequent partial removal.

When sulphur dioxide is added to a must, a portion gradually enters into combination, though the nature of the compound formed does not seem to be definitely known. The reaction is not complete; for any sugar concentration there is a certain value of the ratio of combined to free sulphur dioxide. Rise in temperature favours dissociation of the compound. Since it is the free sulphurous acid which exerts the sterilising action, more has to be added than would be the case if sugar were not present. Free sulphur dioxide can be removed by heating under reduced pressure or by passage of another gas. (Or, what comes to much the same thing, liberation of carbon dioxide during fermentation.) As sulphur dioxide is removed, the compound dissociates, and the free sulphur dioxide thus

produced, removed in turn. (*See* L. Musso, *Bull. de la Soc. Ind. de Rouen*, 1924, No. 6; *Revue Agricole d'Afrique du Nord*, 1925, 7.)

Oil of mustard has been used for sterilising the finished wine, but it has been found that an amount sufficient to effect complete sterilisation renders the wine almost undrinkable.

Selected Yeasts.—The methods of culture and effects of using selected yeasts are discussed.

THE BOUQUET OR FLAVOUR OF WINE.—Whilst certain flavours are desirable, none should be too exaggerated. Defects (as distinct from disease) tend to disappear as the wine matures. Too long a fermentation is liable to exaggerate any defect due to the variety of grape.

The breakage (*Casse, Bruch*) of wine is a turbidity due to interaction of iron salts with constituents of the wine in presence of oxygen. The "Casse" itself is a colloidal combination of iron with products derived from the limited oxidation of tannins and certain wine proteins. Sulphur dioxide added in the form of potassium metabisulphite has a pronounced effect in preventing "Casse." Citric acid also diminishes the tendency to its formation, but tartaric acid has little effect.

The use of ferrocyanide for this purpose has been legalised in Germany.

UTILISATION OF BY-PRODUCTS.—In this section a brief account is given of the methods of utilising the marc, including the recovery of tartaric acid.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Buttermilk or Milk Product in a Mixed Feed by Determination of the Lactose present.—M. R. Coe. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 251–257.)—Dried buttermilk contains proportions of lactose varying from 7·1 to 47 per cent. according to the season of the year and the treatment during manufacture, so that judgment of the amount of buttermilk in a mixed feed from the lactose content gives a very indefinite result. For the determination of lactose in dried buttermilk or dried skim milk or whole milk, the following modification of the picric acid method gives accurate results. The sample, ground to pass a 40-mesh sieve, is washed with 20 c.c. of ether, and 2 grms. are placed in a 300 c.c. measuring flask with 200 c.c. of water, care being taken that no lumps form. The mixture is heated in a boiling water-bath for 30 minutes, with occasional shaking, to dissolve the lactose, cooled and made up to the mark. After the mass has been thoroughly stirred in a beaker to ensure that no lactose remains undissolved and enclosed in globules of casein, albumin, or fat, it is filtered through a double filter-paper on a Buchner funnel to give a clear or opalescent filtrate. A small portion of the liquid is saturated with dry picric acid crystals to precipitate the proteins and to provide the picric acid filtrate

which contains the lactose. To 1–3 c.c. of the picric acid filtrate, introduced into a Nessler tube so that it does not touch the sides, is added 1 c.c. of 22 per cent. sodium carbonate solution, the tube immersed for 15 minutes in a boiling water-bath, and the liquid then cooled and diluted to nearly the same colour as a standard containing 0·0002 grm. of lactose per c.c., 3 c.c. of this standard being heated with 1 c.c. of the carbonate solution in the water-bath with the solution of the sample, and diluted to 30 c.c. Since the colour developed by the addition of alkali changes on standing, a fresh standard is prepared with each batch of samples tested. The colour comparison is made in any good colorimeter.

If the gravimetric determination of the sugars is preferred, 150 c.c. of the clear filtrate from the Büchner funnel are treated, in a 200 c.c. measuring flask, with 10 c.c. of 15 per cent. sodium tungstate solution, 5 drops of thymol blue, and then concentrated sulphuric acid, drop by drop, until the liquid turns pink; 10 drops more of the acid are added to ensure the proper P_H (1·5–2·0). The solution is made up to the mark, left overnight and filtered, and 25 c.c. are taken for the determination of sugar by the Munson and Walker method (*Methods of Analysis*, A.O.A.C., 1925, 190).

If C is the volume to which the 3 c.c. of the resulting solution of the sample is diluted for the tintometer reading, R_1 and R_2, the tintometer readings for the standard and sample respectively, and W the weight (2 grms.) of sample taken, the percentage of hydrated lactose in the sample is given by $\frac{0{\cdot}2\ CR_1}{WR_2}$.

The method used for the determination of lactose in a mixture of feeding stuffs is based on the fact that lactose is not fermented by yeast, and may thus be determined after elimination of the other sugars. The only materials containing interfering substances are cottonseed meal and soya meal. Of the material, ground to pass a 40-mesh sieve, 10 grms. are extracted with ether and then heated with 200 c.c. of water in a 300 c.c. measuring flask in a steam-bath for exactly 30 minutes, with frequent shaking, to dissolve the lactose. The cooled liquid is made up to volume and filtered through a Büchner funnel, and 150 c.c. of the filtrate, together with 20 c.c. or more of alumina cream, made up to 200 c.c. and filtered. Of the clear filtrate, 150 c.c. are boiled in a 300 c.c. Erlenmeyer flask, cooled, mixed with 0·75 grm. of pressed or brewers' yeast, and left to ferment overnight at 25–30° C.; in cold weather at least 2 days may be necessary. The carbon dioxide and alcohol are expelled by boiling, and the liquid treated, in a 100 c.c. measuring flask, with 5 c.c. of 15 per cent. sodium tungstate solution and 5 drops of thymol blue, and with concentrated sulphuric acid until a pink colour appears (plus 10 drops, as before), The solution is made up to 100 c.c., and, if no precipitate forms by the next morning, 10 drops of the sulphuric acid are added and the liquid filtered next day. Of the clear filtrate, 30 c.c. are saturated with picric acid, shaken frequently during 20 minutes, and filtered. Ten c.c. of the filtrate, placed carefully at the bottom of a Nessler tube, are heated with 3 c.c. of 22 per cent. sodium carbonate solution in a steam-bath for 15 minutes, a standard tube, containing 3 c.c. of saturated picric acid

solution in which 0·0002 grm. of lactose per c.c. is dissolved, being similarly treated. When cold, the liquid is diluted to a slightly darker colour than the standard, which is made up to 30 c.c. The percentage of hydrated lactose present is given by $\frac{0{\cdot}008\ CR_1}{R_2}$, and the proportion of buttermilk may then be calculated by use of a suitable factor. T. H. P.

Nutritive Value of Hydrogenated Oils.—S. Ueno, M. Yamashita and M. Ota. (*J. Soc. Chem. Ind. Japan*, 1928, **31**, 92B.)—A comparative study has been carried out on the food value, before and after hydrogenation at 110° to 115°, of sardine, herring, fin-back whale and chrysalis oils. The tests were applied to young healthy rats fed on an artificial ration to which was added 10 per cent. of the particular oil, and it was found that the nutritive values of all four were clearly superior after being hardened. The physical and chemical constants were as follows :

Before hydrogenation.

	Sardine.	Herring.	Fin-back whale.	Chrysalis.
Sp. gr. at 15°/4° C.	0·9299	0·9174	0·9205	0·9232
$n_D^{20°}$	1·4799	1·4712	1·4718	1·4751
M.pt.	—	—	—	—
Acid value	0·23	0·24	0·65	0·39
Saponification value	190·3	187·1	192·9	192·8
Iodine value (Hanus)	166·2	106·6	106·8	135·9
Reichert–Meissl value	0·4	0·7	0·5	0·4
Hehner value	92·4	93·6	93·8	93·3

After hydrogenation.

Sp. gr. at 100°/4° C.	0·8581	0·8555	0·8535	0·8524
$n_D^{20°}$	1·4621	1·4588	1·4589	1·4583
M.pt. °C.	29·6–31·8	31·1–34·7	28·1–31·7	41·3–42·8
Acid value	0·30	0·25	0·28	0·79
Saponification value	190·7	187·0	189·3	192·6
Iodine value (Hanus)	64·2	55·7	64·5	68·6
Reichert–Meissl value	0·3	0·4	0·4	0·4
Hehner value	93·9	93·8	93·7	93·8

R. F. I.

Determination of Citric Acid in Fruits and Fruit Products. B. G. Hartmann and F. Hillig. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 257–266.)—The determination of citric acid as pentabromacetone (ANALYST, 1927, **52**, 549) may be applied to the determination of this acid in fruits and fruit products. Either by diluting or by adding sucrose, a solution of the material is prepared which will contain approximately 25 per cent. of solids, any alcohol present being expelled by evaporation. One hundred grms. of the liquid are heated on a steam-bath for 15 minutes, then treated at once with 5 c.c. of 20 per cent. potassium

hydroxide solution more than the amount necessary for neutralisation. The next morning 40 c.c. of 43 per cent. sulphuric acid solution are added, and the liquid heated to 50° C. on a water-bath for 15 minutes, cooled, made up to 200 c.c. in a measuring flask, and filtered. The citric acid content of 100 c.c. of the filtrate is made up to about 0·1 grm. by dilution or by addition of the acid. The 100 c.c. are mixed in a 500 c.c. Erlenmeyer flask with about 0·3 grm. of purified asbestos and 25 c.c. of a solution containing 50 grms. of potassium bromide per 100 c.c., kept at 48–50° C. for 30 minutes, and treated with 125 c.c. of potassium permanganate solution (5 grms. per 100 c.c.) in three portions in rapid succession, the liquid being shaken after each addition. The temperature is not allowed to exceed 55° C., which is maintained for 5 minutes after the first addition of permanganate, and 30 c.c. of a solution containing 40 grms. of ferrous sulphate and 1 c.c. of concentrated sulphuric acid in 100 c.c. of water are added immediately to remove the manganese dioxide. The liquid is cooled, left, with agitation, in a refrigerator overnight, and decanted on to a thin tightly compressed pad of asbestos on a Gooch crucible, to which the precipitate is transferred by means of a small portion of the clear filtrate. The contents of the crucible are washed at once with three 20 c.c. portions of ice-cold sulphuric acid (1+100) and three 20 c.c. portions of ice-cold water, the precipitate being dried to constant weight over sulphuric acid in a vacuum desiccator protected from strong light. The crucible is weighed and, after the pentabromacetone has been removed by treatment with three 20 c.c. portions of 95 per cent. alcohol and three 20 c.c. portions of ether, again dried and weighed. Multiplication of the weight of pentabromacetone by 0·424 gives the anhydrous citric acid, which is multiplied by 1·14 to correct for loss of the acid. The results obtained by this method for a number of fruits and fruit products are given. Concord grape juice contains 0·04 per cent. of citric acid (*cf.* Nelson, ANALYST, 1925, **50**, 295) and commercial grape aroma essence 0·163 per cent., probably added during manufacture. The tomato and grape fruit juices show larger quantities (0·409 and 1·465 per cent.) than are indicated by titration (0·309 and 1·140 per cent.), so that substantial proportions of the acid are present in the combined form. T. H. P.

The Iron Content of Plant and Animal Foods. W. H. Peterson and C. A. Elvehjem. (*J. Biol. Chem.*, 1928, **78**, 215–223.)—As more data are accumulated it becomes increasingly evident that great variations exist in the mineral content of different samples of the same foodstuff. The iron content of about 150 samples of our common food materials has been determined and the percentage figures are given. These range from 0·00015 per cent. for lemon juice to 0·0192 per cent. for parsley. Arranged in descending order with reference to their iron content the classes of foods come as follows : dried legumes, green leafy vegetables, dried fruits, nuts, cereals, poultry, green legumes, roots and tubers, non-leafy vegetables, fish and fruits. Twenty samples of cabbage varied from 0·00017 per cent. of iron to 0·00059 per cent. Vegetables such as cabbage, celery and head lettuce, which contain little chlorophyll, were found to be low in iron ; thus, a

direct relation between iron content and presence of chlorophyll is evident. The juice of oranges and tomatoes contains less of the total iron than is proportional to the weight of expressed juice ; the iron clings to the solids. Thus, it is desirable to give infants both juice and pulp as early as possible. Salt water fish contain more iron (about 40 per cent. more) than fresh water fish. Fish with dark-coloured tissue contain more iron (about 75 per cent. more) than those with light-coloured tissue. The dark meat of poultry is likewise higher in iron than the light meat.

P. H. P.

Hungarian Paprika. (*Paris Hungarian Legation Official Document* ; *Ann. Falsific.*, 1928, **21**, 210–215.)—Paprika (the fruit of *Capsicum annuum*) may be of several grades, but all contain pericarp and pollen grains. First grade (*a*), paprika precieux-doux, consists of pericarp and washed grains ; (*b*), paprika demi-doux, consists of pericarp, fibrous vessels and washed grains ; (*c*), pink paprika, contains all the parts of the fruit except peduncle ; second (*d*) and third (*e*) are of the same quality as (*c*), but the fruits are not selected. The content of ash and sand as fixed in Hungary is :—(*a*, *b*) ash 6·5, sand 0·5 per cent. ; (*c*) 6·8 and 0·6 ; (*d*) 8·0, 1·0 ; and (*e*) 12·0 and 3·0 per cent. The content of ash in (*c*) may rise to 7·2, and of sand to 0·7 per cent., and for (*d*) to 8·5 and 1·2 per cent. The oil content should be up to 18 per cent. for (*a*), and is normally 14 to 16 per cent. Traces of peduncle may sometimes be found in (*d*) and (*e*), and occasionally a small amount of foreign starch from the sacks used may be present. The colour varies, and the more grains present the darker the red. In a chemical examination of paprika the colour is judged against type samples, water is determined in the water oven, and ash and sand by usual methods ; ether extract by shaking 10 grms. of dried product with 100 c.c. of ether ; crude fibre (20 to 28 per cent.) by König's method ; capsicine by Fodor's method, with the use of acetone and vanadic acid ((*a*) 0·01, (*b*) 0·03–0·04, (*c*) 0·08–p·09 per cent.). Foreign colouring matter is detected by moistening samples on filter paper with distilled water, 85 per cent. alcohol, alcoholic sodium hydroxide, and sulphuric acid and alcohol, when added colouring matter shows as lines and circles. D. G. H.

Pharmacological Assay of Digitalis by Different Methods. J. W. Trevan, E. Boock, J. H. Burn. and J. H. Gaddum. (*Quart. J. Pharm.*, 1928, **1**, 6–22.)—Two samples of digitalis leaf, one strong and one weak, were assayed in comparison with the international digitalis powder by different methods, and satisfactory agreement was obtained for the strong sample but not for the weak. The international standard powder is considered a practical standard for leaf and tincture in Great Britain, but withdrawal of the prohibition by the Geneva Conference of the use of leaf differing from it by more than 25 per cent. is advocated, each country to be allowed to arrange its own methods for standardisation.

D. G. H.

Assay of Alkaloids in Hyoscyamus Leaves. Ph. Fischer. (*Süddeutsche Apoth.-Ztg.*, **68**, 38, 293 ; *Pharm. J.*, 1928, **120**, 592.)—A slight modification of the Swiss Pharmacopoeia process, whereby the alcohol is denatured with methyl

alcohol used in place of rectified spirit, gave good results. Thirty grms. of hyoscyamus leaves and 190 grms. of 70 per cent. alcohol are shaken together for one hour, brought on to a filter, 20 cm. in diameter, and 100 grms. (= 15·2 grms. of leaves) filtered, evaporated to 20 grms., treated with 10 drops of dilute hydrochloric acid, and, after cooling, made up with water to 30·4 grms. Of this, 24 grms. (= 12 grms. of drug) are filtered through a folded paper (10 cm. in diameter), 120 grms. of ether added, and then, after shaking, 3 c.c. of 10 per cent. ammonium hydroxide, and the whole shaken for 15 minutes. After standing 15 minutes, 100 grms. (= 10 grms. leaves) are run through an absorbent wool plug, and the ether evaporated. The residue is dissolved in 2 grms. of alcohol, 5 c.c. of 0·01 *N* hydrochloric acid and 150 grms. of water added, and the liquid titrated with 0·01 *N* potassium hydroxide solution with methyl orange as indicator. Not more than 4·75 c.c. of potassium hydroxide should be used, at least 0·25 c.c. of hydrochloric acid being thus required for neutralising the alkaloids present, corresponding to at least 0·07 per cent. of hyoscyamine. One c.c. of 0·01 *N* hydrochloric acid is equivalent to 0·0289 grm. of hyoscyamine. D. G. H.

Action of Picric Acid on Tropine Silicotungstate. R. Hazard. (*J. Pharm. Chim.*, 1928, **120**, 255–262.)—There is considerable difference in the solubilities of the silicotungstates of atropine and of tropanol, the limit of precipitation of the former being one forty thousandth in a liquid of acidity corresponding to 2 per cent. hydrochloric acid, and of the latter one thirteen- to fourteen-hundredth. If a saturated aqueous solution of picric acid is added to a solution of tropanol silicotungstate a crystalline precipitate is formed quickly or slowly in accordance with the volume, and the quantity is in proportion to the tropanol silicotungstate left in solution. It appears to consist of the tropanol silicotungstate rendered insoluble by the picric acid. The reaction does not occur with atropine, which is insoluble, so that the two bases may be separated, and the presence of tropanol characterised after decomposition of the atropine by hydrolysis. The reaction may be applicable to the silicotungstates of other alkaloids, and a 10 per cent. solution of silicotungstic acid saturated with picric acid is advised in place of Bertrand's reagent for detecting trace of alkaloids. D. G. H.

Assay of Ointments of Mercuric Oxide and Ammoniated Mercury. N. L. Allport. (*Quart. J. Pharm.*, 1928, **1**, 23–27.)—About 5 grms. of yellow mercuric oxide ointment, or 1 grm. of the red, are dissolved by warming to 50° C. in 100 c.c. of a mixture of 13 parts (by vol.) of benzene, 2 of glacial acetic acid, and 5 of 90 per cent. alcohol. Mercuric sulphide is then completely precipitated from the clear solution by means of hydrogen sulphide gas, the solution warmed to 50° C., and the precipitate collected, washed with hot benzene and alcohol, dried at 120° C. and weighed. The weight, multiplied by 0·9309, gives the weight of mercuric oxide. The method, which was found satisfactory, occupied two hours, including 1½ hours for drying. In the case of ammoniated mercury ointment, about 2·5 grms. (or 1·5 of the B.P. 1898 preparation) are dissolved at

70° C. in 100 c.c. of a mixture of 9 parts (by vol.) of benzene, 10 of glacial acetic acid, and 1 of 90 per cent. alcohol; the acetic acid is strong enough to dissolve the white precipitate. The subsequent procedure is as before. D. G. H.

Biochemical.

Perception of Acid Taste. A. Berlatzky and T. Guevara. (*Lancet*, 1928, **214**, 1311.)—The limiting values of P_H for the perception of acid taste are: For sulphuric acid, 2·9; nitric, 3·2; citric, 3·9; tartaric, hydrochloric, and lactic, 4·3; acetic, 4·5; phosphoric, 4·7. Mineral acids, by reason of their greater dissociation and consequent greater hydrion concentration in solutions of equal alkali-neutralising power, are known to have a more markedly acid taste, but it might have been expected that the P_H limit of perception of sourness would be the same for all acids. It is suggested that the negative ions, *e.g.* sulphate and nitrate, have antagonistic action. Sulphate ions have a more depressant action on the nerves than chloride ions, the concentration limit of the bitter taste of magnesium sulphate being higher than that of magnesium chloride. T. H. P.

Quantitative Determination of Mercury in Urine and Faeces, and the Influence of Medication. N. E. Schreiber, T. Sollmann and H. S. Booth. (*J. Amer. Chem. Soc.*, 1928, **50**, 1620–1625.)—The authors' method (ANALYST, 1926, **51**, 477) applied to the determination of mercury in normal urines, gives the same degree of accuracy as with pure solutions of mercury salts. The results are unaffected by prolonged standing without refrigeration and by the presence of arsphenamine, bismuth, chloral hydrate, barbital, and of small amounts of bromides or hexamethylene tetramine, but if iodides or large amounts of bromides are present, complex salts, from which mercury is not precipitable as sulphide, and iodates or bromates are formed, and about 4 grms. of sodium nitrite should be added after oxidation (*loc. cit.*) to liberate the halogen. The excess of nitrite may be oxidised by means of permanganate, and the excess of manganese dioxide then removed in turn by hydrogen peroxide. It is advisable to avoid the administration of aromatic compounds such as sodium salicylate, cinchophen or large amounts of hexamethylene tetramine, since these compounds are not completely oxidised. Faeces are oxidised by potassium permanganate with concentrated nitric acid, in place of sulphuric acid. The fat is filtered from the cool solution when this is yellow in colour, the oxidation then continued till the liquid is colourless, and the excess of manganese dioxide removed by hydrogen peroxide. If, in addition, a spiral of copper wire, slightly oxidised in a flame and then reduced with methyl alcohol, is used to prevent the deposition of free sulphur, 2 to 3 mgrms. of mercury in the daily specimen may be determined, with a loss of 0·01–0·04 mgrm. J. G.

Colorimetric Determination of the Hydrogen Ion Concentration of Blood. V. C. Myers and E. Muntwyler. (*J. Biol. Chem.*, 1928, **78**, 243–255.)—Comparison has been made of the electrometric and colorimetric P_H values of

114 samples of human blood plasma obtained from hospital patients. Electrometric determinations of the P_H at 38° C. and colorimetric determinations at room temperature have been made on 103 samples of blood plasma. The Cullen colorimetric method (*J. Biol. Chem.*, 1922, **52**, 501) was used, the colour comparisons being made with the bicolorimeter essentially as described by Myers, Schmitz and Booher (*J. Biol. Chem.*, 1923, **57**, 209 ; ANALYST, 1923, **48**, 564). Very good agreement between the two methods was obtained, as is indicated by the fact that, when the C correction (P_{Hc} 20° C.–P_{He} 38° C.) 0·22 P_H was used, 59 per cent. of the colorimetric values were within $\pm$0·02 P_H, 74 per cent. within $\pm$0·03 P_H, and 85 per cent. within $\pm$0·04 P_H of the correct value. The C correction for 10 samples of dog plasma averages 0·30 P_H. The colorimetric P_H at 38° C. was compared with the electrometric P_H at 38° C. on 41 samples of plasma. The H correction (P_{Hc} 38° C.–P_{He} 38° C.) averaged $\pm$0·02 P_H, and 59 per cent. of the colorimetric values were within $\pm$0·02 P_H of the true P_H. When the colorimetric P_H obtained at 38° C., which was also determined, was subtracted from the colorimetric P_H determined at room temperature corrected to 20° C., an average was obtained of 0·21 P_H for 51 samples ; thus the major part of the C correction is for the temperature change. Since the P_H of the plasma does not change appreciably on dilution when the P_H of the saline diluent is properly adjusted, it seems likely that possible variations in the C correction may result only as the temperature change is influenced by the character and concentration of the protein present. P. H. P.

Colorimetric Determination of the Hydrogen Ion Concentration of Urine. V. C. Myers and E. Muntwyler. (*J. Biol. Chem.*, 1928, **78**, 225–242.)—A colorimetric method for the determination of the P_H of urine is described in which use is made of the bicolorimeter and the phthalein dyes, phenol red, brom-thymol blue, brom-cresol purple and brom-cresol green. The method is a modification of that of Myers and Booher (*Proc. Soc. Exp. Biol. and Med.*, 1924–25, **22**, 511), devised in an attempt to eliminate possible errors due to the factors of temperature, dilution, salt and carbon dioxide content of the urine. Satisfactory colorimetric readings may be made with the bi-colorimeter on a larger number of urine samples without dilution, but, as this is not always true, the urine is diluted 1:5. When a 1:5 dilution, with a saline diluent set at a definite P_H, rather than with distilled water, is employed, and the determination made under oil, the effect of dilution is stabilised as far as possible, and the loss of carbon dioxide is minimal. The determinations are made at room temperature (25° C.), and, by means of corrections obtained by comparison with the electrometric method, the values are corrected to 38° C. The correction factor for phenol red is 0·24, for brom-thymol blue 0·20, for brom-cresol purple 0·20, and for brom-cresol green 0·22 P_H. In a study of 67 urine specimens, in which the P_H ranged from 4·9 to 7·2, the above corrections brought the colorimetric determinations within 0·05 P_H of the correct value of the undiluted specimen at body temperature in 80 per cent. of the determinations. Consideration has been given to the effect of salt on the indicator, and its possible interference in the determination of the P_H in urine is discussed.

As the salt concentration increases above $M/15$ the colorimetric value is greater than the electrometric, whilst with concentrations less than $M/15$ the reverse is true. Although it may seem troublesome to prepare saline solutions for each indicator, it saves time where many determinations are to be made, for, with special bottles, the saline solutions, once adjusted, will keep for considerable periods. P. H. P.

The Complex Nature of Vitamin *B* as found in Wheat and Maize. **C. H. Hunt.** (*J. Biol. Chem.*, 1928, **78**, 83–90.)—Previous experiments seemed to show that wheat grain contains the antineuritic vitamin, and only a small amount of another vitamin which, in conjunction with the antineuritic factor, induces growth. Further information has now been obtained in regard to the nature of the vitamin *B* in wheat and also in maize. The conclusion of Sherman and Axtmayer (*J. Biol. Chem.*, 1927, **75**, 207) that vitamin *B* is composed of at least two fractions has been confirmed, and their terminology has been adopted for this paper ; *viz.*, the antineuritic factor is called vitamin *F*, and the growth or antipellagra factor, vitamin *G*. Rats on a vitamin *B*-free diet, supplemented with 0·3 to 2·0 grm. of autoclaved yeast, died in 5 to 9 weeks with polyneuritis or emaciation. The autoclaving of the yeast destroyed vitamin *F*. When the growth of rats which were receiving a mixture of either wheat or maize and autoclaved yeast is compared with the growth of other rats which were receiving wheat or maize alone, it is seen that the autoclaved yeast supplements the value of wheat and maize in inducing growth. Thus in wheat and maize the limiting factor for growth is vitamin *G*, which is, in this case, found in autoclaved yeast. If sufficient vitamin *G* is present, 15 per cent. of wheat in the diet furnishes about the minimum amount of vitamin *F* for growth. Therefore the vitamin *B* complex is composed of at least two vitamins : one which prevents polyneuritis in rats (vitamin *F*) and a second factor (vitamin *G*), which prevents experimental pellagra and, together with vitamin *F*, induces fair growth in rats. Wheat and maize contain approximately the same amount of vitamins *F* and *G*, but they are richer in vitamin *F* than in vitamin *G*. Vitamin *G* is thermostable, whilst vitamin *F* is thermolabile. Yeast contains both the vitamins *F* and *G*, and possibly a third factor which is now being investigated. P. H. P.

Assay of the Antirachitic Vitamin *D*. **K. H. Coward.** (*Quart. J. Pharm.*, 1928, **1**, 27–33.)—The Pharmaceutical Society has adopted a particular sample of irradiated ergosterol as a standard for measuring the antirachitic vitamin *D*, and it is proposed to define the unit of antirachitic potency as the amount of activity contained in 0·0001 mgrm. of the standard. It is of such potency that a daily dose of not more than 0·0001 mgrm. will, under the conditions of the test, cause complete healing of the induced rickets, and it is believed that samples of similar potency can be prepared whenever required. The test is based on the "line" test of McCollum, and is described by Steenbock and Black (*J. Biol. Chem.*, 1925, **64**, 263). A cod-liver oil assay involved doses each of 0·00025, 0·0005, 0·001, 0·0025, 0·005 grm. of oil to 5 rats, and 0·00001, 0·000025, 0·00005,

and 0·0001 mgrm. of irradiated ergosterol to four others. Two finely graded series of results showed that 0·005 grm. of oil gave complete calcification, as did both the two highest doses of ergosterol, and 0·00001 mgrm. of irradiated ergosterol was equal to 0·001 grm. of oil; 0·000025 to 0·0025; and 0·00005 mgrm. to 0·005 grm. of oil; so that a dose of 10 mgrms. of the oil was equal to the Society's unit of 0·0001 mgrm. of irradiated ergosterol, and the antirachitic potency of the oil is expressed as 100 units per grm. If the substance to be tested contains enough phosphorus to alter the Ca:P ratio materially, further comparison should be made with some substance containing equal amounts of phosphorus but no vitamin *D*. D. G. H.

Quantitative Comparison of the Antirachitic Factor in Human Milk and Cow's Milk. J. Outhouse, I. G. Macy and V. Brekke. (*J. Biol. Chem.*, 1928, **78**, 129–144.)—With the advent of the study of experimental rickets in animals, various attempts have been made by different workers to evaluate the antirachitic potency of human milk and cow's milk, and conflicting results have been obtained, owing to differences in experimental technique. A more detailed comparison has now been made of the antirachitic properties of human milk and cow's milk which have been produced under definite conditions and given to rats with an experimental technique somewhat modified from the heretofore approved methods. On a modified Osborne and Mendel synthetic rachitogenic ration, growth and appetite of rats have been satisfactory. Rickets has developed as early as 14 to 21 days. By variations of the calcium and phosphorus content of the ration, it has been possible to maintain an approximately constant ratio of calcium : phosphorus = 5 throughout the rickets-developing period and the curative period of milk feeding. Data are presented which show that human milk, given in amounts of 25, 30, or 40 c.c. daily, contains, for rats, no antirachitic factor. Under the same carefully controlled conditions, 30 c.c. of cow's milk, given daily for 7 days, induced marked healing of rachitic lesions in rats. Since the calcium : phosphorus ratio was controlled, the curative properties of cow's milk are not due to the large percentage of calcium and phosphorus present in the milk. This factor in cow's milk is analogous to the bone-calcifying properties of cod-liver oil. As rats do not consume human milk with avidity, the human milk was condensed under partial vacuum to about a third of the original volume.

P. H. P.

Bacteriological.

Bactericidal Action of Dyes. A. Philibert and J. Risler. (*Compt. rend.*, 1928, **186**, 1583–1584.)—When defibrinated human blood containing diphtheria organisms, *Streptococcus*, *B. coli*, or *Staphylococcus* is exposed in glass tubes to the luminous rays corresponding with the absorption spectrum of haemoglobin, the first three organisms grow freely and the last only slowly on re-inoculation. If, however, 10 c.c. of the blood are sensitised by addition of 1 drop of methyl violet solution (1 : 10,000), the bacteria are almost immediately destroyed, this action

being rendered still more rapid if the sensitised blood is irradiated. Experiments with guinea pigs show that the shock produced by the introduction of certain dyes in solution is tolerated by the animals, and it thus appears possible to conceive of a simple chemo-therapy by the selective action of dyes and of a secondary chemo-therapy by sensitisation to light rays of extremely long wave-length.

T. H. P.

Isolation of Bacillus Typhosus from Sewage and Shellfish. W. J. Wilson. (*Brit. Med. J.*, 1928, 1061–1062.)—The examination of sewage for the presence of *B. typhosus* may be conveniently made by means of Wilson and Blair's medium (glucose, sulphite, iron, bismuth, and brilliant green) (*J. Hygiene*, **1927**, **26**, 374), the efficiency of which depends on the facts that (1) *B. typhosus* in presence of a fermentable carbohydrate is able to reduce a sulphite to a sulphide and so form a black colony with an iron salt; and (2) bismuth sulphite in presence of a certain excess of sodium sulphite suppresses the growth of most coliform bacilli, this selective action being intensified if brilliant green also is present.

When 0·5 to 1 c.c. of sewage is poured over the surface of a plate of the medium and allowed to dry, incubation at 37° C. for 24 hours results in the development of black colonies with a metallic halo and of pale green colonies of *B. proteus*. It is among the black colonies that *B. typhosus* is sought. If sub-cultured on MacConkey or Endo medium, all the black colonies are found to be non-lactose fermenters, so that such media do not allow of distinction between *B. typhosus* and other reducing bacteria. On the other hand, many of the black colonies simulating those of *B. typhosus* are sucrose fermenters, use of a modified Endo medium containing sucrose thus indicating the typhosus colonies. The principal organism forming the black colonies on the bismuth sulphite medium is named *B. effluvii*, and occurs in most samples of sewage, but has not yet been found in faeces.

Four samples of sewage, taken in February and March, 1928, from the combined sewage of the upper and lower level sewers of Belfast on its way to the sedimentation tanks, were examined as above. In the first sample, of 31 black colonies, 4 were of non-sucrose fermenters and all of these typhoid colonies; for the other samples, the numbers of black colonies were respectively 67, 64 and 71, the numbers of non-sucrose fermenters, 7, 14 and 15, and the numbers of typhoid colonies, 2, 7, and 8. Belfast was once badly typhoid-infested, and would be expected to contain many typhoid "carriers." Of nine black colonies isolated from cockles collected from the foreshore of Belfast Lough, two proved to be non-sucrose fermenters, and one of these *B. typhosus*. T. H. P.

Organic Analysis.

Improvements in the Method of Elementary Organic Analysis. A. Wahl and J. P. Sisley. (*Compt. rend.*, 1928, **186**, 1555–1558.)—When the old copper oxide combustion method is used for organic substances, if only 0·08 to 0·1 grm. of the material is taken, a tube 55–60 cm. in length suffices, and the

combustion may be completed in 25 to 45 minutes. If a halogen or sulphur is present and the copper oxide has to be replaced by calcined lead chromate, the time required is prolonged to 40 to 70 minutes. In all the determinations made, the substance was placed in a boat, and the tube was finally swept out with a current of dry oxygen. T. H. P.

A General Reaction of Amino Acids. H. D. Dakin and R. West. (*J. Biol. Chem.*, 1928, **78**, 91–105.)—During an attempt to prepare diacetylcystine, a reaction which appears general to α-amino acids was discovered, and is described. When amino acids are warmed with acetic anhydride and pyridine, carbon dioxide is evolved and two acetyl groups are introduced, one attached to nitrogen and one to carbon. The compounds have the general formula $R.CH.(NH.COCH_3).CO.CH_3$, and are derivatives of acetylaminoacetone. Proof of the constitution of the products is adduced, and various derivatives are described, as well as their conversion into glyoxal and pyrazine derivatives. Proline and alkylamino acids do not react analogously, but undergo simple acetylation. The same is true of α-amino-hydratropic acid, which contains no unsubstituted hydrogen in the α position. The reaction between α-amino acids, pyridine and acetic anhydride has certain analogies to a change observed by W. H. Perkin, senior (*J. Chem. Soc.*, 1886, **49**, 317), who heated acetic anhydride and sodium acetate at high temperatures and obtained acetone. Propione and butyrone were similarly obtained. It is believed that β-ketonic acids represent intermediate stages of the reaction, and are then decomposed into the ketone and carbon dioxide. The function of the pyridine in the reaction appears to be catalytic, and is not shared by dimethylaniline or quinoline; yet pyridine derivatives, such as lutidine, collidine and nicotinic acid, were effective. The reaction is not limited to amino acids, but is shared by α-halogen acids and some unsubstituted acids, such as phenyl-acetic acid which gives methylbenzylketone. The possible biological significance of the reaction is discussed, together with reference to the possible uses of alkyl acetaminoacetones for the preparation of pharmacologically active substances. The ketones derived from tyrosine and phenylalanine were well characterised crystalline products, and those obtained from other amino acids, including leucine, β-trimethylalanine, glycine, alanine, histidine and glutamic acid, were readily converted into crystalline derivatives. P. H. P.

Determination of High-boiling Phenols in a Coal Tar Creosote and Castor Oil Soap Disinfectant. J. N. Taylor. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 222–225.)—High-boiling phenols in an emulsion-producing type of disinfectant containing a castor-oil soap may be determined more satisfactorily by direct distillation than by distillation in a current of steam. The procedure suggested is as follows: Fifty grms. of the disinfectant, 2·5 grms. of sodium hydrogen carbonate and 0·5 grm. of magnesium carbonate are placed in a 250 c.c. Pyrex distilling flask, the sides of which are washed down with 50 c.c. of a high-boiling refined petroleum distillate previously washed with alkali. Distillation is conducted slowly over a naked flame through a Liebig condenser the distillate being

collected in a Weiss, type 2, measuring tube until it attains a deep yellow colour. The water collecting in the tube is transferred to a separating funnel, and any phenols present salted out, taken up in kerosene and added to the rest of the distillate, which is washed with 10 c.c. of 10 per cent. sulphuric acid solution and measured, without the acid washing liquor, at 25° C. The phenolic bodies are then removed by treatment with successive 80 and 60 c.c. portions of 10 per cent. sodium hydroxide solution, and, after thorough draining, the final volume in the tube again noted at the same temperature. Duplicate determinations on a prepared disinfectant gave diminutions in volume of 11·95 and 12·03 c.c., corresponding with 25·3 and 25·4 c.c. per 100 grms. of disinfectant, the actual amount present being 25·6 c.c. T. H. P.

Studies on Gossypol. IV. Apogossypol. E. P. Clark. (*J. Biol. Chem.*, 1928, **78**, 159–166.)—Gossypol is converted into formic acid and apogossypol, a new phenolic substance, when it is treated with 40 per cent. sodium hydroxide at the temperature of the steam bath for 30 minutes. These substances are produced in the proportion of 2 molecules of formic acid to 1 molecule of apogossypol. Apogossypol has the molecular formula $C_{28}H_{30}O_6$, and is formed by the elimination of the two carbonyl groups of gossypol as formic acid. It is a colourless crystalline material with no definite melting point, and is soluble in ordinary organic solvents, and the solutions thus formed darken more or less quickly, according to the nature of the solvent employed. It dissolves freely in dilute alkali, from which it is precipitated by carbon dioxide ; its alkaline solutions darken at once, and rapidly acquire a purple colour. Even crystalline apogossypol is so unstable that exposure of the dry crystals to the air and light for a few hours causes them to change to a jet black powder. The fact that the elimination of the two carbonyl groups from gossypol causes the characteristic yellow colour of the substance to disappear substantiates a previous suggestion made that the chromophores of gossypol are carbonyl groups. All the 6 oxygen atoms of apogossypol are present as hydroxyl groups. The phenol accordingly forms a hexacetyl derivative and a hexamethyl ether by the replacement of the hydroxyl hydrogens by acetyl and methyl radicals. These compounds are described. In the hexaacetate, as in hexaacetyl gossypol, two of the acetyl groups are more resistant to hydrolytic agents than the remaining four. The direct determination of the methoxy groups in the hexamethyl ether could not be made, since the material was entirely inert in boiling hydriodic acid as used in the Zeisel method. The toxicity of apogossypol was determined and found to be much less than that of gossypol. The lethal dose, given intraperitoneally to white rats, was found to be from 60 to 75 mgrms. per kilo of body weight. Apogossypol differs from gossypol in its physiological action in causing acute toxic effects only ; no chronic toxic effects follow the administration of small doses. P. H. P.

Quantitative Determination of Methyl Glyoxal by means of an Alkaline Solution of Iodine, and its Chemical Mechanism. F. Fischler and R. Boettner. (*Z. anal. Chem.*, 1928, **74**, 28–32.)—About 20 c.c. of a 2·5 per cent.

solution of methyl glyoxal are well stirred with a known excess of a 0·1 *N* iodine solution for 30 minutes in the presence of a large known excess of 0·1 *N* sodium hydroxide solution. The precipitated iodoform is filtered off, washed and weighed, and the calcium determined in the total filtrate by precipitation as oxalate in the presence of acetic acid. The residual iodine is titrated in another portion of the solution with 0·1 *N* solution of sodium thiosulphate after the addition of a known amount of 0·1 *N* hydrochloric acid sufficient to neutralise the alkali and provide an excess of about 25 per cent., the excess of acid being then titrated with standard alkali, with phenolphthalein as indicator. Under these conditions, in the presence of an excess of OH' ions, the reaction is $CH_3CO.CHO+4OI'=CHI_3+C_2O_4''+I'+OH'+H_2O$, and since, according to the equation $4I_2+8OH'=4I'+4OI'+4H_2O$, 4 hypoiodite ions are equivalent to 8 atoms of iodine, 1 c.c. of 0·1 *N* iodine solution is equivalent to 0·0009 grm. of methyl glyoxal. The amount of alkali produced during the reaction is determined from the back-titration of the added acid, and, since 8 atoms of iodine cause the production of 1 c.c. of 0·1 *N* alkali, a check is provided. The greatest observed errors were +0·07, − 0·07 per cent. for the oxalate and iodoform methods, respectively. J. G.

Colour Reactions of Logwood, Sappan, and Sanders Wood. A. A. Wilson and J. N. Bennett. (*Pharm. J.*, 1928, **120**, 582.)—Characteristic colour reactions are obtained with alcoholic solutions of logwood, sappan and sanders wood, and ferric chloride, copper sulphate, ferrous sulphate, and particularly lead acetate. Sappan gives a pink to magenta colour, logwood a blue precipitate, and sanders wood a deep red solution. Sappan yields amounts of extractive varying with the sample, so that one per cent. tinctures may give colours from pink to magenta. If one drop of dilute hydrochloric acid is subsequently added, sappan and logwood colours are destroyed, but sanders wood colour is almost unaffected. D. G. H.

Determination of Sulphato-groups in Chrome Leather. H. B. Merrill, J. G. Niedercorn and R. Quarck. (*J. Amer. Leather Chem. Assoc.*, 1928, **23**, 187.)—A method has been worked out for determining separately in undried chrome leather the proportion of sulphuric acid (SO_4) combined with the collagen molecule and that combined with the chromium atom. The procedure is as follows :—Two grms. of the leather are treated with 100 c.c. of water, rotated for 1 hour and left over-night. Next day 2 drops of methyl red (0·5 per cent. solution) are added, and then sufficient 0·02 *N* sodium hydroxide solution to raise the P_H value of the aqueous extract to 5·2–5·4 (change of colour to a salmon-pink). The flask is rotated for 15 minutes and, if necessary, the solution is again adjusted to P_H 5·2 to 5·4, after which, if necessary, it is readjusted at 15 minute intervals for the first 2 hours, and at half-hourly intervals for the rest of the day. Then, after standing for a second night, it is readjusted at hourly intervals until about 48 hours have elapsed since the beginning. The solution is now poured off, the leather washed with distilled water for 1 hour, and the sulphate ion remaining in the leather determined by the phosphate displacement method (*J. Amer. Leather*

Chem. Assoc., 1920, 504), and recorded as chromium-bound sulphate. The total sulphate ion is determined by the phosphate displacement method on a fresh sample. The difference between the total and the chromium-bound SO_4 is taken as being combined with collagen. In one example the weight (per 100 grms. of dry leather) of sulphuric acid combined with collagen was found to be 1·33 grms., and that combined with chromium 4·49 grms. Perfect accuracy for the method is not claimed, owing to a small proportion of the sulphate ion combined with chromium being removed together with that combined with collagen, but the error is probably under 10 per cent. The method is useful, however, in showing the changes in percentage acidity of the sulphato-chromi-complex during neutralisation, and is superior to the pyridine method of Gustavson (*J. Amer. Leather Chem. Assoc.*, 1927, **22**, 60), which gives results wholly misleading. R. F. I.

Quantitative Determination of Lead in Organic Compounds. H. Gilman and J. Robinson. (*J. Amer. Chem. Soc.*, 1928, **50**, 1714–1716.)—About 0·5 grm. of sample is heated, gently at first, with 7·5 c.c. of concentrated sulphuric acid in a Pyrex beaker till white fumes are evolved. Concentrated nitric acid (1 to 3 c.c.) is then added in small portions to the cooled solution, which is heated after each addition, and finally, after dilution with water, to remove the nitric acid. The lead sulphate in solution is precipitated in the cold with 150 c.c. of water and 100 c.c. of 95 per cent. alcohol, filtered through a Gooch crucible, washed with 10 per cent. sulphuric acid and then with 95 per cent. alcohol till neutral, dried for 1 hour at 110° C. and weighed. The method has been used successfully for the analysis of various aryl and aryl-alkyl lead compounds. J. G.

Inorganic Analysis.

Pinachrome as a One Colour Indicator. I. M. Kolthoff. (*J. Amer. Chem. Soc.*, 1928, **50**, 1604–1608.)—Pinachrome (*p*-ethoxyquinaldine-*p*-ethoxyquionoline-ethylcyanine), which is a weak base slightly soluble in water, but soluble in hydrochloric acid to give a colourless solution at P_H 5·4 and a weak red-violet colour at P_H 5·6, is recommended as an indicator for P_H determinations between P_H 5·8 and 7·8. It has practically no " salt-error " for low concentrations of electrolytes, though for high concentrations it indicates too acid a reaction. It is particularly suited for P_H determinations of tap or distilled waters, and for these and other unbuffered liquids it should be used neutral, 100 mgrms. being dissolved in 40 c.c. of alcohol, 1·9 c.c. of 0·1 *N* hydrochloric acid added, and enough water to make 100 c.c. It behaves as a mono-acid base with a colourless action, and has a high temperature-coefficient, since between 20° and 40° C. $P_H = 7{\cdot}34 + 0{\cdot}013\ (20° - t)$. The colour change is not instantaneous, and at least 2 minutes and less than 1 hour should elapse before the comparison is made. Alkaline solutions should be mixed without shaking. J. G.

Potentiometric Determination of Gallium. H. D. Kirschman and J. B. Ramsey. (*J. Amer. Chem. Soc.*, 1928, **50**, 1632–1636.)—A solution of gallium trichloride may be titrated potentiometrically with 0·05 *M* potassium

ferrocyanide solution in the presence of potassium ferricyanide (added with the former in order to prevent decomposition), with an accuracy of about 0·2 per cent. Neutral or slightly acid solutions gave the most satisfactory curves, and a temperature of $40\pm2°$ C. was selected to compromise between decomposition of gallium ferrocyanide at high temperatures and the slow rate of reaction at low temperatures. The curves were unaffected by a 16-fold variation in the amount of ferricyanide. The ratio of gallium to ferrocyanide in the precipitate is 1·333, corresponding with the formula $Ca_4(FeCy_6)_3$, and the precipitate differs from the ferrocyanides of zinc and of indium, to which the method has also been applied (*ibid.*, 1927, **49**, 2739), in that it is not of a complex nature. The ferrocyanide solution may be standardised against metallic zinc. J. G.

Specific Reagent for the Rapid Gravimetric Determination of Sodium. H. H. Barber and I. M. Kolthoff. (*J. Amer. Chem. Soc.*, 1928, **50**, 1625–1631.)—The reagent (at least ten times the volume of the test solution) is prepared as previously described (ANALYST, 1927, **52**, 304), and well mixed with a solution in about 1 c.c. of water of not more than 8 mgrms. of sodium. It is filtered at the same temperature after 30 minutes, washed 10 times with 2 c.c. of reagent, the excess of which is removed by 5 washes with 2 c.c. portions of 95 per cent. alcohol previously saturated with the precipitate, and then dried by means of ether and weighed at once. The precipitate has the formula $(UO_2)_3ZnNa(CH_3COO)_9$, $6H_2O$, and the factor 0·01495 gives the weight of sodium with an accuracy of 0·5 per cent. It forms water-soluble tetrahedrons, which in the hexahydrated form are very stable at room temperatures. Ammonium salts, zinc, small amounts of barium, calcium or magnesium, and less than 50 mgrms./c.c. of potassium chloride do not interfere, but lithium and strontium and large amounts of potassium (especially in the form of sulphate) give precipitates. Phosphates and organic acids also interfere. J. G.

Zirconium Sulphate as a Reagent for the Detection of Potassium. R. D. Reed and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1928, **50**, 1515–1522.)—Concentrated solutions of zirconium sulphate may be used for the detection of 0·53 mgrm. or more of potassium (as sulphate) in the absence of sodium, and 1·76 mgrm. in its presence, the solutions being mixed in 1 c.c. portions, shaken and immersed in ice-water if no precipitate appears after 1 hour at room temperature. The walls of the test-tube should be rubbed with a glass rod at intervals to promote precipitation, but if 18 mgrms. or more of potassium are present, a deposit forms at once. The interfering effect of sodium sulphate is greatest for solutions richest in potassium. If long enough is allowed for precipitation, the test is almost as delicate as Bray's sodium cobaltic nitrite reaction (*ibid.*, 1909, **31**, 611), though the sensitiveness of the latter may also be increased by extending the precipitation period. Dilution of the reagent to 10 per cent. increased its sensitiveness for from 1·76 to 0·7 mgrm. of potassium in the presence of sodium. It is always advisable to carry out a blank test as a control. J. G.

Determination of Tellurium. L. Moser and R. Miksch. (*Monatsh. für Chem.*, 1923, **44**, 335–349.)*—The published methods for the determination of tellurium were investigated ; the best gravimetric methods are, weighing of the metal obtained by the simultaneous action of hydrazine hydrochloride and sulphur dioxide, and hydrolytic precipitation of tellurous acid and ignition to TeO_2. The following modifications of volumetric methods were found serviceable:—*Stannous Chloride* (Brauner).—The solution of the dioxide in hydrochloric acid (1:5) is reduced in a graduated flask filled with carbon dioxide by a measured excess of stannous chloride : $TeCl_4+2SnCl_2=Te+2SnCl_4$. The flask is closed, and shaken for 5 minutes in a boiling water-bath, cooled quickly, and the volume made up with air-free water. When the precipitate has deposited completely, an aliquot volume of solution is titrated with iodine. *Dichromate.*—The hydrochloric solution of the dioxide is diluted and treated, drop by drop, with sodium hydroxide until faintly cloudy. A small excess of 0·1 *N* dichromate solution is added, and the oxidation completed in a boiling water-bath (10 minutes). After cooling in running water, the solution is titrated—without having been acidified—with ferrous ammonium sulphate solution containing a little sulphuric acid ; external ferricyanide indicator. *Permanganate.* (Brauner.) Titration in acid solution gives high results, but the following procedure in alkaline solution is satisfactory. The alkaline tellurite solution is treated with a measured excess of permanganate and warmed for some time. It is then cooled to 10° C., and acidified with dilute sulphuric acid which is slowly stirred in ; an excess of 0·1 *N* oxalic acid is then added, after which the solution is heated to 50° C. and titrated with permanganate. A fair excess of permanganate (30 c.c. of 0·1 *N* solution for 0·1 grm. TeO_2) is required. Gooch and Peters' procedure (*Z. anorg. Chem.*, 1899, **21**, 405) is accurate.

Re-investigation of the methods for the separation of tellurium and selenium led to the following conclusions : *Fusion with potassium cyanide* is unreliable ; the process is only of historical interest. *Volatilisation of selenium tetrabromide* (Gooch and Peirce) gives accurate results, but chlorides interfere ; in practice, however, the two elements are almost invariably present as chlorides. *Differential precipitation with sulphur dioxide* in strongly acid solution after Keller is a good method provided hydrazine hydrochloride is added to the solution. Browning and Flint's *hydrolytic precipitation method* is very good : the authors dilute the faintly acid chloride solution with a large volume of boiling water, render it slightly ammoniacal against methyl orange, and re-acidify with a few drops of acetic or formic acid. Tellurous acid is precipitated in crystalline form ; selenium is recovered from the filtrate by known methods. A new method described by the authors is based on the *reduction of selenious acid by hydriodic acid.* The solution containing selenious and tellurous acids is added, drop by drop, to a boiling acidified solution containing 4 times the potassium iodide required for the formation of the tetraiodides. The selenium is precipitated in the black, crystalline form, not in

* As this and the three following Abstracts are of great analytical importance, the Publication Committee has decided to publish them, notwithstanding the fact that the original papers appeared some years ago.—EDITOR.

the red colloidal modification which adsorbs iodine. Rapid addition of the solution may cause a high result, which can be corrected by more prolonged drying at 105° C. to constant weight. Tellurium is determined in a separate portion by hydrolysis. W. R. S.

Separation of Zirconium and Hafnium from Titanium, Cerium, and Thorium. L. Moser and R. Lessing. (*Monatsh. für Chem.*, 1924, **45**, 323–337.)—The separations are based on the precipitation of zirconium and hafnium as arsenates. Hafnium arsenate is proved to be more insoluble than the zirconium compound ; hence it is necessarily precipitated therewith. The presence of hafnia in the zirconia employed was established by fractional precipitation of the arsenates and calculation of the mean equivalent weight of the oxides in the fractions on the basis of their arsenic content ; the first fraction had an equivalent of 98·68, the third 95·03, and the thirteenth 90·56. Chloride solutions are precipitated as normal $Zr_3(AsO_4)_4$ with a variable amount of water ; strongly acid nitrate solutions give $ZrO.HAsO_4$. The latter is the more stable salt. (1) *Zirconia-hafnia from titania.*—The hydroxides precipitated by ammonia are carefully washed with hot water and dissolved in 50 c.c. of nitric acid (1 vol. of sp. gr. 1·4 and 3 vols. of water), and 5 c.c. of 3 per cent. hydrogen peroxide. The boiling solution is stirred and precipitated with a small excess of 20 per cent. disodium hydrogen arsenate solution ; after 10 minutes' boiling, the precipitate is allowed to settle on a water-bath and the clear liquid decanted ; the precipitate is washed by decantation with the 1:3 nitric acid, then on the filter with hot water till acid-free. The wet filter and precipitate are ignited at very low temperature ; the precipitate is transferred to a distillation flask, and the crucible washed with strong sulphuric acid, in which the precipitate is dissolved together with 2 grms. of hydrazine sulphate. Hydrochloric acid is added through a dropping-funnel, at first drop by drop, then more rapidly. When the bulk of the arsenic has been distilled, 50 c.c. of hydrochloric acid and 2 grms. of sodium bromide are added, the stopper being lifted for a moment ; the flask is immersed in a briskly boiling water-bath, and a vigorous current of air conducted through the liquid, with addition of 20 c.c. of strong hydrochloric acid at intervals of 10 minutes. In one hour all the arsenic is obtained in the distillate, which is titrated with bromate. The zirconia is precipitated in the residual liquor by ammonia ; the precipitate is dissolved in hydrochloric acid, the precipitation repeated, and the precipitate ignited and weighed. The filtrate from the zirconium arsenate is treated with sufficient sulphurous acid to destroy the hydrogen peroxide ; the titania is obtained by double precipitation with ammonia. The zirconia may also be computed by difference. (2) *Zirconia-hafnia from ceria.*—The arsenate method is an alternative to oxalate precipitation. The solution of the nitrates in nitric acid (1 to 3 water, as under (1)), free from other acids, is boiled with 10 c.c. of 3 per cent. hydrogen peroxide : ceric nitrate, if present, is reduced. The precipitation is carried out as in the preceding case ; the ceria in the filtrate is likewise obtained by double ammonia precipitation, and the precipitate ignited to CeO_2. (3) *Zirconia-hafnia from thoria.*—Glaser's oxalate

and Delafontaine's fluoride methods are not highly accurate. The arsenate method will give good results if the acidity is strictly regulated. The mixed ammonia precipitate is dissolved in nitric acid of the strength specified above under (1); the paper is washed with the same acid. The filtrate (100 to 120 c.c. for 0·2 grm. of oxides) is boiled and precipitated, drop by drop, with 20 per cent. disodium arsenate till no further precipitate forms. The hot solution is filtered, the precipitate washed with the dilute nitric acid, then with water to neutral reaction. The thoria in the filtrate is precipitated with ammonia, the precipitate washed with hot water, dissolved in hydrochloric acid (1:1), and the resulting solution precipitated with hydrogen sulphide. The arsenic sulphide is removed by filtration, and the filtrate again precipitated with ammonia; the precipitate is ignited to ThO_2. Thoria being more basic than ceria or titania, the ammonia precipitate produced in the filtrate from the arsenate precipitate contains arsenic acid, hence the hydrogen sulphide treatment. The zirconium arsenate precipitate is gently ignited and treated by distillation as under (1), or (Zr, Hf)O_2 taken by difference.

W. R. S.

Determination of Thallium as Chromate. L. Moser and A. Brukl. (*Monatsh. für Chem.*, 1926, **47**, 667–683.)—Thallium is most usually weighed as the iodide, in spite of the fact that salt filters poorly, has a tendency to form colloidal solutions, and is far too soluble for quantitative purposes. The authors discard the determination as iodide and recommend thallous chromate as the most suitable compound for gravimetric work (Browning and Hutchins, *Chem. News*, 1899, **80**, 226). Its solubility was found to be 0·0427 grm. per litre for water, 0·0092 for 60 per cent. alcohol, and 0·0060 for a solution containing 2 per cent. of ammonium hydroxide, 4 per cent. of potassium chromate, and 10 per cent. of alcohol. The feebly ammoniacal liquid is boiled and stirred during the addition of potassium chromate solution, the excess of which should yield an approximately 2 per cent. solution. The yellow precipitate is allowed to stand 12 hours, filtered by decantation on a porous crucible, and washed with one per cent. potassium chromate, then 50 per cent. alcohol, with due regard to the removal of adsorbed potassium chromate. It is dried at 120° C. and weighed. Methods are described for the separation of thallium as chromate from lead, manganese, aluminium, iron, chromium, zinc, cadmium, nickel, cobalt, silver, mercury, copper, bismuth, arsenic, antimony, tin, and selenium.

W. R. S.

Separation of Caesium, Rubidium, and Potassium. L. Moser and E. Ritschel. (*Z. anal. Chem.*, 1927, **70**, 184–189.)—As a result of a re-investigation, the authors reject as unreliable the separation methods for the three alkali metals published by Strecker and Diaz (ANALYST, 1926, **51**, 162). The paper contains the experimental evidence on which the authors' opinion is based.

W. R. S.

Determination of Ferrocyanide. P. P. Budnikoff. (*Z. anal. Chem.*, 1928, **73**, 433–438.)—The processes used for the examination of commercial potassium ferrocyanide were re-examined. The gravimetric methods are unreliable or

tedious. Of the volumetric precipitation methods, the most widely used is titration with a solution of zinc salt. The uncertain end-point with an external indicator constitutes the weakness of this method; de Haën's permanganate titration was found to be an accurate process. The ferrocyanide solution to be titrated should not be stronger than 0·05 *N*, otherwise a milky precipitate of $K_2MnFe(CN)_6$ masks the end-point. The cold solution is titrated after addition of 10 c.c. of 20 per cent. sulphuric acid. W. R. S.

Physical Methods, Apparatus, etc.

The Lovibond Colour System. 1. A Spectrophotometric Analysis of the Lovibond Glasses. K. S. Gibson, F. K. Harris and I. G. Priest. (*Scientific Paper No.* 547 *of the Bureau of Standards, Washington, D.C.*, Feb. 1927, pp. 1–46.)—According to the Preface (by I. G. P.) the present paper is the first of a series on the colorimetric standardisation of the Lovibond Tintometer glasses, with special reference to their use in the oil trade, which have the object of eliminating inconsistencies between the glasses and enabling a particular colour to be specified in reproducible colorimetric terms, free from the personal equation. Three variables (dominant wave length, purity and integral transmission, corresponding with hue, saturation and brilliance, respectively) are required for the full representation of a colour, and calibration has been achieved by expressing each of these as a function of the Lovibond number of the series of glasses. The smoothed curves thence obtained are used for the elimination of inconsistencies and for the standardisation of unknown glasses. It is considered that lack of uniformity in the glasses is not the principal cause of discrepancies in the colour grading of oil, and that this may possibly arise from differences in the apparatus, source of illumination and personal factor of the observer. The number of separate glasses in a particular combination is also a factor, since the loss of light by reflection makes it possible to match the same colour by different combinations of glasses unless a system such as that of Bailey (*Amer. Oil Chem. Soc. J. Oil and Fat Industries*, 1925, **2**, 8) is adopted. The spectral transmissions from 380 to 750mμ, and the integral transmissions for sunlight of the 60 unit glasses from 1·0 to 20·0 of the red, yellow and blue series (also yellow 35·0) of the Bureau of Standards' set, and of their neutral (red+yellow+blue) combinations are presented in the form of tables and curves. These show that, apart from erratic variations, the glasses conform to Lambert's law of transmission, $-\log T_\lambda = kN + b$, where T is the transmission at a given wave-length, N the Lovibond number (or in general, the thickness of absorbing material), and k and b are constants depending on the spectral density and on the loss of light by reflection, respectively. In the case of combinations of the composition of about (35 yellow+7 red) used in the oil trades the maximum deviations from ideal grading for a number of glasses between 7·1 and 7·6 were of the order of 0·5 of a red unit, and occur for about 1 in 10 or 20 of the glasses, whilst irregularities of about 0·1 are more common. The method enables the red in such combinations to be standardised to within 0·1, the degree

of accuracy required for such measurements being about 0·2 to 0·3. In general, similar conclusions were obtained from the examination of the set of standards used by the American Oil Chemists' Society. J. G.

Reviews.

FOODS: THEIR COMPOSITION AND ANALYSIS. By the late A. WYNTER BLYTH and M. WYNTER BLYTH. Seventh edition, revised and partly re-written by H. E. COX, M.Sc., Ph.D., F.I.C. Pp. xxv+619, with 4 plates and 90 illustrations. London: C. Griffin & Co., Ltd. 1927. Price 38s. net.

Eighteen years have elapsed since the sixth edition of this well-known work was published. In the meantime much new knowledge of the analytical chemistry of foods has become available, and official Regulations and Orders governing the sale and composition of foods have been issued at an unprecedented rate. For these reasons an extensive revision of many parts of the book was found necessary by Dr. Cox, who has had an unenviable task, owing to the well-known difficulty of dovetailing new work into the pattern of an old book of another's authorship. This should be borne in mind as regards any criticism made here. The revision might, in a future edition, be advantageously carried much further, as there remains in the book much almost obsolete matter, and later references in some of the sections would be helpful. In view of the time which has elapsed since the last edition, the work of deletion and re-arrangement cannot have been easy, and, on the whole, the reviser has accomplished it with much circumspection and discrimination. The book remains a valuable guide on its subject, and the comments on the work which follow are made by the reviewer with the object of increasing the usefulness of the volume in any future edition.

The work is divided into nine parts, with 3 Appendices and an adequate Index. Part I comprises the history of Adulteration in this and other countries. It contains material of much interest, and might be still further extended. The last 20 pages of this part are concerned with the present law regarding adulteration, and contain a fairly complete account of the latest Regulations relating to condensed and dried milks, preservatives and colouring-matters, etc. Probably owing to the time of publication of the work, however, the important Part I of the First Schedule of the Preservatives Regulations is not in its final and complete form, while these regulations should of course be cited as the Public Health (Preservatives, etc., in Food) Regulations, 1925–27, and not 1925–26, as stated in the Contents (p. ix). The chief Acts relating to foods are given in the second Appendix.

Part II (Introductory) deals with special apparatus used in the analysis of foodstuffs, and with a description of the microscope, spectroscope and camera as applied to the chemistry of foods. It would be an advantage if the use of tintometers were included here, as well as a description of the methods and apparatus employed in the determination of the hydrogen-ion concentration of

liquids. Some guidance as to modern books on microscopy should also be given, the references being restricted to publications of forty or more years ago. The section on the detection of coal-tar and other colours by chemical reagents and by the spectroscope is good. In the description of the Kjeldahl method, reference is made to the addition of potassium bisulphate at a certain stage of the process, but it is more usual to employ the neutral sulphate.

Part III (Carbohydrates) comprises in its 90 pages a discussion of the chemistry of the Starchy and Saccharine substances of foods. The section on the methods of determination of various sugars in admixture is commendably practical and concise, although one does not readily get used to the reviser's terms "positive" and "negative" as applied to the rotation of sugars, either a dextro-rotation or a laevo-rotation being surely a positive result.

Some of the sections on individual foods are all too short, and might usefully be amplified. In connection with the detection and determination of preservatives in jams, it should be mentioned that formaldehyde might occur as a natural product of the boiling of fruit and sugar.

When persulphates are present in flour, it is stated that the application of an alcoholic solution of benzidine to a mixture of the flour and water, made into a paste, gives rise to brown spots in the mixture; but the spots of persulphate are coloured *blue* by this treatment. There is an interesting series of paragraphs relating to the occurrence of moulds and other foreign growths in bread, but no mention is made of the state known as "ropiness" in bread, a condition so prevalent in certain breads during the late war, and due to the presence of the *Bacillus mesentericus*.

Part IV treats of Milk, Cream, Butter and Cheese. The article on the first-mentioned food is overloaded with obsolete matter and requires more thorough revision. In connection with colouring matters in milk, it should be noted that the Public Health (Milk and Cream) Regulations, 1912–17, are now revoked, but that the addition of colouring matters to milk is prohibited by the Milk and Dairies (Amendment) Act, 1922. One misses in the article on Milk any mention of the later work on the composition of cows' milk, as, for example, that embodied in Tocher's book on the "Variations in the Composition of Milk." A critical review of this subject, and of the precise value of the refractometric characters of milk-serum, would be of great value at the present time to all who have to do with the analytical examination of milk. The newer methods for the determination of boron compounds in milk and other foods, due to the Government Laboratory and Monier-Williams, are not mentioned.

No work on foods of this character can to-day be considered complete without at least some slight treatment of the subject of "Vitamins." Neither under "Butter," however, nor elsewhere in this volume, is there any mention of these elusive, but interesting and important, compounds. Apart from this omission, the section on "Butter" is a fairly comprehensive account of its chemistry and analysis. One again misses, however, the critical guidance one might expect regarding the value of certain of the "constants" obtained in the course of an analysis, such as, for example, in the case of the "baryta value." It is now known

that some butters (notably Irish butter) may, at least at certain seasons of the year, yield positive values of considerable extent in the Avè-Lallemant process. On page 296, in the description of Richmond and Harrison's method for the determination of boric acid in butter (line 3), a necessary part of the method is accidentally omitted; and on p. 304, the word "altered" should be "filtered." The article on Cheese is too short to be useful to analysts, and contains no statement as to the proper amount of fat to be expected in a whole-milk cheese, though a table of representative analyses is given.

Parts V and VI deal with Tea, Coffee and Cocoa, and with Alcohol, Spirits, Wines and Liqueurs. The latter part contains the latest methods for the determination of arsenic in beer, malt and other substances. The methods for the detection of the various foreign colouring-matters in factitious wines are well set out. Parts VII and VIII treat shortly of Vinegar, Lime and Lemon Juices, Spices and Condiments, etc., and contain a useful series of monographs on these foods. The volume concludes with an exhaustive treatment in Part IX of the analytical chemistry and bacteriology of Waters, together with an Appendix of tables and reagents relating to water analysis.

By the deletion of obsolete matters and the extension of the articles on various foods, as indicated in this review, the usefulness of the work as a practical manual for chemists would be greatly increased. Yet, within its present limits, the book is a reliable guide to the subjects on which it treats, and one may hope that the revision now begun may be continued, so that chemists may have "Blyth's Foods" before them for many years to come in its up-to-date form. The work is well bound and printed, and contains few typographical errors. Many useful illustrations of the microscopical characters of seeds, leaves and grains, etc., are contained in the volume. ARNOLD R. TANKARD.

THE CHEMISTRY OF LEATHER MANUFACTURE. By T. A. WILSON, Chief Chemist, A. F. Gallum & Sons Co. (Tanners), Milwaukee, Winsconsin. Second Edition. Volume I. Pp. 495. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc. New York. 1928. Price $10.00.

The first English edition was published in one volume appearing in 1923, and was followed by translations into German (1925), French (1926) and Russian (1927). In its various editions it has thus spread over the entire leather world. The fact that there is a demand for a greatly enlarged second English edition is in itself the best recommendation for this work.

The first volume, so far published, deals with such divers subjects as the histology and the chemistry of the skin, the physical chemistry of the skin, the physical chemistry of the proteins, the micro-organisms and enzymes met with in the tanning industry, the preservation and disinfection of the skin, the different methods of treating the latter preparatory to tanning (fleshing, unhairing, bating, drenching and pickling), and the vegetable tanning materials, their qualitative and quantitative analysis, as well as their chemistry. This is an heroic effort, especially when one considers that Mr. Wilson is the Chief Chemist of the largest

tannery in the world. It is, therefore, not surprising that some of the chapters are not quite up to academic standards as required by the specialists of each of the many branches dealt with by the author. Thus, for example, in the sections dealing with the chemistry of the proteins the classical researches of Zelinsky on the constitution of the proteins are omitted, the chapter dealing with enzymes does not account for the many far-reaching investigations of Euler, and in the section devoted to the chemistry of the tannins this subject is mainly dealt with in the light of Freudenberg's work on it.

However, in spite of these disadvantages, Mr. Wilson must be congratulated on a most valuable addition to the literature, by which he has far surpassed all that has hitherto been written on the subject. M. NIERENSTEIN.

CHEMICAL ENCYCLOPAEDIA. AN EPITOMISED DIGEST OF CHEMISTRY AND ITS INDUSTRIAL APPLICATIONS. By C. T. KINGZETT. 4th Edition. Pp. vii+808. London: Ballière, Tindall & Cox. 1928. Price 35s. net.

In the course of only eight years this book has passed through three editions and it has grown considerably in bulk. The object of the author in writing this work is to provide, in an easily accessible form, concise information on chemistry and its industrial applications. The information is presented in a form which is useful both to academic and works chemists. Testimony to the great success which has attended the author in his work is amply supplied by the fact that a fourth edition of his books should have been found necessary in so short a period. The present edition contains 200 pages more than the preceding edition, which are devoted to the more technical side of chemistry, namely, to chemical engineering, chemical plant, chemical industry, commercial applications of chemistry and chemical products. Much information is to be found in the book, not only on pure and applied chemistry, but also on mineralogical subjects.

The information contained in this book is accurate and very clearly put forward; and although the book has the form of a dictionary, the material is very readable. The book is well produced, and printers' errors are rare. A new feature in the present edition is the inclusion of references to the original and other literature, from which the reader may obtain fuller information.

Apart from a few very minor changes, which could with advantage be made in one or two of the definitions, the reviewer can find little to criticise; the book is an admirable production which can be recommended with confidence.

JAMES F. SPENCER.

THE CHEMISTRY OF CHEMOTHERAPY. By G. MALCOLM DYSON, Ph.D. Pp. 272, 4to. London: Ernest Benn, Ltd. 1928. Price 32s. 6d. net.

The term chemotherapy is now being used in at least two senses. Its inventor, Ehrlich, employed it to describe treatment of disease by chemicals, which were specifically parasiticidal. As Ehrlich initiated the whole business and left behind him ideas which are still fruitful, it would seem desirable that his view should be respected.

The term seems, however, to have appealed to many people as a useful portmanteau word to signify both chemistry and therapeutics, and there has recently

been a tendency to extend its meaning far beyond the limits imposed by Ehrlich. The book now under review affords a fresh example of this extension, but, as the author nowhere attempts to define chemotherapy, it is not possible to say whether he belongs to the portmanteau school, or, like Sir Almroth Wright, has arrived, on etymological grounds, at the conviction that the name chemotherapy belongs "by right to every form of chemical treatment." Only about one-fifth of this book deals with chemotherapy in Ehrlich's sense, and the rest would be more appropriately described by a more general title.

The book is divided into ten chapters, of which the first is headed "Physiological Action and the Nature of Matter." Though the contents of this chapter are less impressive than its title, they do give an interesting and stimulating account of our present knowledge, or rather lack of knowledge, of how drugs act.

It is perhaps excusable for a chemist to take a lofty view of the contribution chemotherapy is likely to make to the welfare of humanity, but surely it is going too far to say that "through the course of civilisation, man, as an animal, is growing less resistant to infection, and has come, and in future will come more, to rely upon externally synthesised medicaments for the combating of infection." Dr. Dyson could no doubt justify this pessimistic view of the effect of civilisation on man's capacity for resisting infection, by quotations from experts, but experts are apt to stress the particular and ignore the general. Such general evidence as is available seems to indicate that, on the whole, civilised man is a healthier and longer-lived animal than either his primitive ancestor, or his contemporary, uncivilised or less civilised brother. The second part of Dr. Dyson's proposition is even less tenable, for there can be no doubt that chemotherapy is a stop-gap, destined to disappear as the progress of preventive medicine and sanitary engineering make it possible to eliminate the means whereby parasites thrive and spread. Even now, such diseases as hookworm and malaria could probably be "stamped out," as Dr. Dyson puts it, if money could be found to give the preventive medical officer and the sanitary engineer a free hand. Chemotherapy may flourish for many a long day to come, but the whole tendency of modern work points to its ultimate supersession.

In the same chapter the author is very severe on "the looseness of thought and even of experimental technique found widely among investigators in physiological, pathological and pharmacological laboratories," to which he traces, among other things, the fact that "the literature teems with contradictions." The waywardness of biological experiments is the constant theme of tribal jokes between chemists and biologists, but the chemist with experience of this kind of work knows that some, at least, of these anomalies are due to pharmacologists working with impure materials supplied by chemists.

In the remaining nine chapters, in which the author deals *seriatim* with the pharmacological action of the principal classes of organic compounds, a good account is given of what is known of the pharmacology and therapeutics of pure organic chemicals, and Dr. Dyson may be congratulated on having compressed into so small a space such a large amount of readable information. He slips rather frequently, *e.g.* in quoting for muscarine (p. 115) a formula which Dr.

King's work on this base shows to be untenable, and by giving Pshorr's formula for morphine (p. 180) and ignoring the recent work on this subject of Gulland and Robinson, Wieland and others. The definition of glucosides given on p. 30 would exclude some of the best known glucosides, such as amygdalin. It is, to say the least, doubtful if santoninoxime is "often used" in place of santonin. Some of the most interesting points dealt with in the various therapeutic notes might have been made more impressive by fuller knowledge of clinical results, but here Dr. Dyson suffers, like everyone else interested in such work, from the fact that clinical results appear in such a diversity of places that it is extremely difficult in many cases to connect the chemical, pharmacological and clinical work on a particular substance. Thus one of the organic mercury compounds (Table XX, p. 249), which Dr. Dyson says "has not been applied directly to any problem of medicine," has in fact been converted into a lipoid-soluble derivative, and is being used in medicine, a point which adds interest to his note on lipoid-soluble mercury compounds (p. 252).

The book ends with a sort of peroration in which the author foresees the production by chemotherapeutical investigation of substances comparable with the enzymes and immuno-compounds, bodies immensely active but non-toxic to man, of which he regards "Baeyer 205" as perhaps a crude forerunner. This seems to be an expression in technical terms of man's almost instinctive belief that naturally-produced substances may be at once potent and harmless. There are numerous examples to the contrary, and in this connection it is interesting to note that the first faint suggestions are beginning to appear in the medical press that even vitamins may produce harmful effects, so that in due course it may prove desirable to abate some of the current enthusiasm for sunshine, either "free" or "bottled."

T. A. HENRY.

A GUIDE TO THE LITERATURE OF CHEMISTRY. By E. J. CRANE and A. M. PATTERSON. Pp. 438. New York: Wiley; London: Chapman & Hall. Price 25s. net.

There can be no question as to the value of this work to everyone who has occasion to consult chemical literature, and the compilers may be congratulated on the thoroughness with which they have done their task. The subject-matter is dealt with in a series of chapters which comprise: Books, Periodicals, Patents and other sources of information, Indexes, Libraries and Procedure. Each chapter is subdivided to facilitate reference to any particular point, and there are excellent name and subject indexes. Throughout the work useful hints are given as to the course to be adopted to obtain the special information required and for its effective use when found. It is interesting to learn from the chapter on Periodicals that there are only three journals devoted to analytical chemistry, *viz.* THE ANALYST for the British Empire, the *Zeitschrift für analytische Chemie* for Germany, and the *Annales de Chimie Analytique* for France.

This is an excellent example of the class of books which Charles Lamb labelled *biblia abliblia*—books which have no claim to be termed books from the literary point of view, although, like railway guides, they are frequently indispensable.

EDITOR.