THE ANALYST

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

Standards for Jams.

THE Council of the Society has had under consideration the action that should be taken by Public Analysts with regard to jams which bear the name of a fruit or fruits, but do not bear the descriptive labels agreed upon with the Food Manufacturers' Federation (ANALYST, **1930**, **55**, 694), *i.e.* jams which bear neither the "full fruit" nor the "lower fruit" standard label.

The fruit content of "full fruit" jam has been accepted by the Council as the minimum amount of fruit which should be present in an article sold, without qualification, as "jam," the word "jam" being used in conjunction with any named fruit. It follows that any named fruit jam containing a lower proportion of fruit than this should, for the information of the purchaser, be suitably labelled. The "lower fruit standard" declaration provides for such a jam, and provides also for the requisite information being given to the purchaser.

The Council is of opinion that any jam which

(1) contains less of the named fruit or fruits than the proportions specified for that jam in the full fruit standard specification, and

(2) is sold without a declaration disclosing its lower fruit content,

should, for the purposes of the Food and Drugs (Adulteration) Act, 1928, be deemed to be deficient in fruit.

The Determination of the Hydroxyl Content of Organic Compounds: Estimation of Castor Oil.

By S. MARKS, M.Sc., A.I.C., AND R. S. MORRELL, M.A., PH.D., F.I.C.

(*Read at the Meeting, February* 4, 1931.)

THE object of this investigation was to discover a reliable method for the determination of the hydroxyl (–OH) content of several complex compounds of oily consistence which had been isolated in the course of the oxidation of β-elaeostearin from tung oil (Morrell and Marks, *J. Oil and Colour Chem. Assoc.*, 1927, **10**, 197; 1929, **12**, 183; *J. Soc. Chem. Ind.*, 1931, **50**, 29; *cf.* ANALYST, 1929, **54**, 503). The usual process of acetylation followed by hydrolysis with potassium hydroxide, or a modification of this process, could not be employed, because (1) the compounds under investigation were decomposed by alkali, and (2) their behaviour, on being heated, was uncertain, and it was, therefore, necessary to conduct the estimation at the lowest possible temperature; if possible, at room temperatures.

The methods recommended by André (*Chem. Umschau*, 1925, **32**, 177) and by Verley and Bölsing (*Ber.*, 1901, **34**, 3354) were first examined, using castor oil, which consists mainly of the glyceride of the hydroxy acid, ricinoleic acid, and which should give approximately 5·2 per cent. of –OH content.* The results given by both these methods at various temperatures were low and discordant. Investigation of the modification of Bölsing's process put forward by Peterson and West (*J. Biol. Chem.*, 1927, **74**, 379) was satisfactory. This consists in treating the hydroxyl compound under examination with a mixture of excess of acetic anhydride and pyridine; the excess of acetic anhydride is titrated with alkali. The following compounds were examined by this process to test its suitability: (i) Castor oil, dried over exsiccated sodium sulphate; (ii) β-naphthol (A.R.); (iii) vanillin, recrystallised (m.pt. 80° C.); (iv) guaiacol, redistilled (b.pt. 202° C.).

About 2 grms. of a mixture consisting of 1 part of acetic anhydride and 3 parts of pyridine were added to 0·5 to 1 grm. of the compound in a pyrex flask. After standing for the periods and at the temperatures set out in the table below, the reaction product was washed into a beaker with ice-cold water and titrated rapidly with $N/2$ potassium hydroxide solution and phenolphthalein.

* Pure triricinolein $(C_{18}H_{33}O_3)_3C_3H_5$ requires 5·47 per cent. of –OH.

The table shows some of the results obtained.

DETERMINATION OF HYDROXYL CONTENT.

Substance.	Temperature. °C.	Duration.	Result. Per Cent.	Calculated.
(1) Castor oil	room	24 hours	5·1	about 5·2
	37	24 ,,	5·1	
	100	15 minutes	5·0	
(2) β-Naphthol	room	48 hours	11·7	11·8
	37	24 ,,	11·8	
	100	15 minutes	11·6	
(3) Guaiacol	room	24 hours	10·4	13·7
	,,	120 ,,	13·5	
	37	24 ,,	11·3	
	100	15 minutes	13·3	
(4) Vanillin	room	24 hours	10·8	11·2
	,,	120 ,,	11·2	
	37	24 ,,	10·6	
	100	15 minutes	11·2	
(5) Methyl ester of oxidised β-elaeostearic acid, $C_{18}H_{28}O_6(CH_3)_2$ ..	37	120 hours	4·6	4·6
	37	48 ,,	4·0	
	room followed by 50	48 ,, 18 ,,	4·7	
(6) Ditto, after hydrogenation, $C_{18}H_{30}O_5(CH_3)_2$	37	120 ,,	4·3	4·7
	room	120 ,,	4·0	

Examination of the figures shows that: (*a*) Castor oil and β-naphthol are comparatively readily acetylated, and ordinary room temperatures can be employed. Castor oil was, therefore, used as a control in the examination of the new oily compounds of unknown constitution, referred to above. The period of exposure was 120 hours, as this apparently sufficed for all the substances examined.

(*b*) Castor oil, β-naphthol, guaiacol and vanillin give satisfactory results by immersion in boiling water for 15 minutes (Verley and Bölsing, *loc. cit.*). This process, therefore, becomes available for the rapid determination of the purity of these substances, and of others which are not decomposed when heated. The method is particularly valuable for castor oil, which is distinguished from other fixed oils by its remarkably high hydroxyl content. The method is much more rapid and simpler than the determination of the acetyl value by the ordinary procedure.

CHEMISTRY DEPT.,
CENTRAL TECHNICAL COLLEGE,
BIRMINGHAM.

The Investigation of Japanese Beeswax.

By HARUICHI IKUTA.

(*Read at the Meeting, March* 4, 1931.)

Since the report of Brodie (*Annalen*, 1848, **67**, 180) there have been published about 140 papers dealing with the properties and constituents of beeswax, but, with few exceptions, these were mainly concerned with European beeswax, and hitherto there have been only two reports on Japanese beeswax, one by Shibasaki (Analyst, 1915, **40**, 549) and the other by Ueno (Analyst, 1915, **40**, 345). According to the investigations previously made, the differences in general properties between Oriental and European beeswaxes were considered to be due to the species of bee, but this had not been established. Ueno confirmed this theory by the results of his experiments on Corean and Ogasawara beeswaxes (*J. Chem. Ind., Tokyo*, 1918, **21**, 319). At the present day, the species and distribution of bees are as follows:

No.	Species of Bee.	Geographical distribution.
1	*Apis dorsata*, Fabricius, 1793	India, Java, Malayan Peninsula, Borneo.
2	*Apis florea*, Fabricius, 1787	
3	*Apis indica*, Fabricius, 1798	East India, China, Japan, South Sea.
4	*Apis mellifica*, L., 1761	Europe, Africa, America.

The oriental beeswax (both Indian and Chinese), which is known by the name of "Ghedda Wax," is secreted by the first three species mentioned above (Nos. 1, 2 and 3). The genuine Japanese beeswax is secreted by the Japanese honey-bee (*Apis indica*, Fab., var. *Japonica*, "Rads.," 1887), which occurs only in Japan and Corea, and closely resembles the oriental beeswax in its chemical and physical characteristics. During the last fifty-five years, however, European beeswax, produced by bees of species No. 4, which had been imported from Hawaii and America in 1876, 1879 and 1899, has also become a Japanese product, and recently this species has been widely and increasingly distributed throughout Japan. On the other hand, in consequence of certain difficulties in culture and of the poor yield of honey, the Japanese honey-bees have lately very much decreased; it is even said they will soon cease to exist, owing to the competition of the European bees.

For this reason, I have made an investigation of the characteristics and composition of the original Japanese beeswax, while there is still the opportunity.

NATURE OF SAMPLES.—The following table gives the districts in Japan where the samples were collected, the appearance of the sample as received, its floral origin, and the appearance of the purified wax derived from it. The wax, separated from the comb by melting with boiling water and straining through calico, was boiled several times with water to remove all soluble impurities, and was finally separated, filtered and dried at 100° C.

TABLE I.

Sample No.	District from which sample was collected.	Appearance of sample as received.	Appearance of purified wax.	Species of bee.	Artificial comb.	Floral origin.
1	Matsuyama	Clear yellow	Almost white	Doubtful	None	Doubtful
2	Iyo	Black honeycomb	Clear orange	Japanese	,,	Orange, haze tree
3	Wakayama	Brown	Pale brown	Doubtful	Present	Obscure
4	Itami	Yellow	Almost white	Italian	,,	Rape, clover, orange
5	Ogasawara	Yellow	Pale yellow	,,	None	Wild plant
6	Sado	Yellow honeycomb	Yellow	,,	Present	Rape, plum, camellia
7	Osaka	Dark brown	Brown	Cross-breed	,,	Doubtful
8	Miyazaki	Yellow	Pale yellow	Doubtful	Doubtful	,,

No cross-breed between the Japanese and the European honey-bee can be produced, and, therefore, a cross-breed of honey-bee in Japan must be obtained with *Apis mellifica*, L. (mainly Italian and Carniolan).

GENERAL PROPERTIES.—In the following table, the acid and saponification values were determined by Bohrish and Kürschner's modified process (*Pharm. Zentralbl.*, 1910, [25], 20), and the acetyl value was derived from Cook's formula (*J. Amer. Chem. Soc.*, 1922, **44**, 392):

$$\text{A.V.} = \frac{V' - V}{1 - \lambda V 10^{-3}}$$

where V is the saponification value of original wax, V′ the saponification value of the acetylated wax, and λ the ratio; that is,

$$\frac{C_2H_2O}{KOH} = 0{\cdot}7488.$$

The determination of the unsaponifiable matter was effected by taking the mean values found by the method of Donath (Grün, *Analyse der Fette und Wachse*, Vol. I, 207) and of Leys (*Chem. Zentralbl.*, 1912, ii, 456).

TABLE II.

Sample No.	Sp. gr. (d_4^{100}).	Melting point. °C.	n_D^{70}, calculated to n_D^{40}.	Acid value.	Ester value.	Saponification value.	Ratio No.	Iodine value (Wijs).	Acetyl value.	Unsaponifiable matter. Per Cent.
1	0·8168	64·5–65·0	1·4557	7·5	75·6	83·1	10·1	11·3	20·7	58·3
2	0·8232	65·0–65·5	1·4560	5·4	79·2	84·6	14·5	14·0	18·7	56·5
3	0·8148	62·0–62·5	1·4552	16·4	83·4	99·8	5·1	8·2	12·2	50·5
4	0·8152	62·5–63·0	1·4554	18·6	74·5	93·1	4·0	9·9	12·4	48·6
5	0·8141	62·5–63·5	1·4554	19·8	74·0	93·8	3·7	8·5	13·1	49·5
6	0·8132	62·0–62·6	1·4546	19·4	74·1	93·5	3·8	7·2	14·4	48·6
7	0·8108	62·5–63·0	1·4545	15·5	73·0	88·5	4·7	9·7	10·9	51·2
8	0·7980	61·5–62·5	1·4535	9·7	52·7	62·4	5·4	7·6	11·4	68·2

For comparison with these figures, constants of oriental beeswax, as recorded by different observers, are given in the following table:

Wax.	Sp. Gr.	Melting point.	Acid value.	Ester value.	Saponification value.	Ratio No.	Iodine value.	Authority.
Apis florea								
max.		68	8·9	123·8			11·4	Hooper, *Agric. Ledger*, 1904 (7).
min.	—	63	6·1	80·8			6·0	
mean	—	64·2	7·5	95·6			8·0	
Apis dorsata								
max.	—	67	10·2	97·8			9·9	
min.	—	60	4·4	69·5			4·8	
mean	—	63·1	7·0	89·4			6·7	
Apis indica								
max.	—	64	8·8	95·9			9·2	
min.	—	62	5·0	84·0			5·3	
mean	—	63·2	6·8	89·6			7·4	
East Indian								
max.	—	63·5	8·9	99·5	106·1	14·9	9·3	Berg: Lewkowitsch, II, p. 924.
min.	—	62·5	6·3	86·2	93·6	10·0	7·1	
mean	—	63·0	7·0–7·5	89–94	96–101·5	12·5–13·5	8·5–8·7	
Indian	(d_{15}^{15})							Roberts and Islip (ANALYST, 1922, **47**, 246).
mean	0·9652	61·4	5·8	92·1	97·9	16·7		
Japanese	(d_{15}^{100})							
max.	0·8207	66·5	8·19	95·14	103·34	14·6	14·14	S. Shibasaki (ANALYST, 1915, **40**, 549).
min.	0·8135	64·9	5·61	80·45	86·35	11·19	10·18	
mean	0·8160	65·9	6·40	83·44	89·85	13·14	12·27	
Corean	(d_4^{100})							
max.	0·8358	66·0	7·7	81·34	87·72	17·63	12·93	S. Ueno (ANALYST, 1915, **40**, 343).
min.	0·8090	65·0	4·46	74·24	79·24	10·23	10·04	
mean	0·8229	65·6	5·85	78·71	84·56	13·45	11·41	

The following remarks may be made regarding the constants of the Japanese beeswax:

Sample No. 1. The employment of artificial comb in the collection of this

sample is doubtful, but, in view of the general properties, this wax would have been considered to be genuine Japanese beeswax.

No. 2. In obtaining this wax no artificial comb was employed, and the constants for this sample agree approximately with those previously attributed to genuine Japanese beeswax.

Nos. 5 and 6. These samples were secreted by European bees (Italian honey-bee), and, therefore, they have the normal constants of European beeswax.

Nos. 3, 4 and 7. These samples, as they have a somewhat high ratio number, are not pure European beeswax, like Nos. 5 and 6.

No. 8. Taking into consideration all the results, such as low specific gravity, melting point, saponification value and refractive index, and high percentage of unsaponifiable matter, the conclusion must be drawn that this sample of wax is adulterated with a large quantity of hydrocarbon.

ARTIFICIAL COMB.—Seventy-three years have passed since the invention of artificial comb by J. Mehring, in 1857, and, at the present day, having regard to the economic and cultural points of view, no one can afford to dispense with its use.

In the earliest years of the invention, artificial combs were prepared from a mixture of beeswax and beeswax substitutes. At first, ceresin was used for this purpose, but, at present, paraffin wax or stearic acid has taken its place, and such a product must, of course, be looked upon as adulterated. Therefore, it is important, in an investigation of beeswax, that the wax taken as sample should be tested for impurities at the outset, otherwise the outcome will be an inaccurate report. For instance, I examined an artificial comb in the case of sample No. 4 (Table II), and its analytical values were as follows:

Sp. gr. (d_4^{100})	0·8193	Iodine value (Wijs) ..	7·2
M.pt. (°C.)	64–64·5	Unsaponif. matter (per cent.)	55·6
Ref. index (n_D^{40})	1·4552	M.pt. of unsap. matter ..	75–76° C.
Acid value	10·7	M.pt. of sap. matter ..	54–55° C.
Ester value	88·9		
Saponif. value	99·6		
Ratio number	8·3		

From the above results it will be seen that the artificial comb of No. 4 consisted of pure beeswax, or of a mixture of beeswax and some other wax. According to my investigation, the wax of No. 4 contained about 10 per cent. of artificial comb, and, therefore, if we calculate the properties of beeswax No. 4, which contains 10 per cent. of artificial comb, the acid, ester and saponification values will be, respectively, 19·4, 73·0 and 92·4, and the ratio number 3·8. These constants agree approximately with the constants of genuine European beeswax No. 5, which did not contain artificial comb.

PROPERTIES OF SAPONIFIABLE SUBSTANCES.—I saponified 20 grms. of the sample with 50 c.c. of *N*-alcoholic potash and 20 c.c. of benzene in a special separation flask. When the saponification was completed, hot water was added, and the boiling was continued under a reflux condenser for a few minutes. The soap solution was drawn off while hot, and was treated with benzene three times, and the saponifiable substances were then separated in the usual manner by boiling with acid. These saponifiable substances were considered to be adulterated with large quantities of fatty acids and very small quantities of resinous matters and unsaponifiable matters. The constants of these saponifiable substances are shown in the following table:

TABLE III.

Sample No.	Melting point °C.	Neutralisation value.	Iodine value.	Mean molec. weight.
1	54 to 55	187·2	9·1	299·2
2	49·5 to 50·5	188·5	10·1	297·6
3	57 to 58	184·5	7·8	304·1
4	58 to 59	182·2	8·7	307·9
5	57 to 57·5	176·5	7·2	317·8
6	57·5 to 58	180·1	7·2	311·5
7	56·5 to 57	172·1	9·6	326·0
8	58 to 59	170·5	7·5	329·0

PROPERTIES OF UNSAPONIFIABLE MATTER.—The unsaponifiable substances separated from saponifiable matter were white or pale yellow solid masses. Their characteristics were as follows:

TABLE IV.

Sample No.	Melting point. °C.	Saponification value.	Iodine value.	Acetyl value.
1	73·5 to 74·5	3·8	10·6	91·0
2	74·5 to 75·4	3·5	17·1	93·8
3	72·5 to 73·1	3·3	9·3	91·5
4	72·5 to 73	4·5	8·4	90·0
5	74 to 75	3·1	8·4	90·4
6	74 to 74·6	3·2	6·8	90·5
7	72 to 72·5	2·5	10·7	82·5
8	69 to 69·6	1·8	9·1	50·6

PROPERTIES OF WAX-ALCOHOL AND HYDROCARBONS.—To separate the unsaponifiable hydrocarbons in beeswax from the alcohols, I used the method of Leys (*Chem. Zentralb.*, 1912, ii, 456), as adopted in the technical standard analysis of oils and fats in Germany (*Chem. Umschau*, 1929, 207). The principle of this method is based on the insolubility of the hydrocarbon in a mixture of fuming hydrochloric acid and amyl alcohol, in which wax-alcohol is soluble. This method of separation is not chemically exact, but, as it is simple, and yields the wax-alcohol without any change, it is convenient in practice.

The results are given in the following tables:

TABLE V.

Sample No.	Wax-alcohol: Melting point of alcohol. °C.	Acetate: Melting point. °C.	Acetate: Saponification value.
1	76·5 to 77	62·5 to 63	112·4
2	77 to 77·6	62·5 to 63·2	114·3
3	74·5 to 75·5	69 to 61	110·8
4	75 to 75·5	61 to 61·5	110·1
5	75·5 to 76	63 to 63·5	113·6
6	75 to 75·5	62 to 63	108·1
7	75 to 76	61 to 62	109·5
8	74 to 75	61·5 to 62	119·8

TABLE VI.

Sample No.	Hydrocarbons: Melting point. °C.	Hydrocarbons: Iodine value (Wijs).
1	65 to 66	17·4
2	64·5 to 65	26·7
3	64 to 65	14·8
4	63·5 to 64·5	16·3
5	62·5 to 63	17·2
6	63 to 64	15·4
7	63 to 63·5	14·2
8	64 to 64·5	9·1

The value given by Lewkowitsch (*Oils, Fats and Waxes*, I, 617) for the acetyl value of the beeswax alcohols, namely, 99 to 103, seems to be erroneous, as the theoretical value for myricyl alcohol is 116·7, and that of ceryl alcohol is 132·3. According to investigations hitherto made (*J. prakt. Chem.*, 1912, **86**, 184), beeswax contains myricyl and ceryl alcohols, but East Indian wax contains only ceryl alcohol. The melting point and iodine value of the hydrocarbons are given respectively as 49·5 to 59·2° C., and 20 to 22 by Lewkowitsch (*loc. cit.*). For these reasons, it will be clearly seen that the wax-alcohol and hydrocarbons of the foregoing tables were still not perfectly separated. However, further investigations on this problem are in progress.

SUMMARY.—The results obtained appear to indicate that:

1. The differences in general properties between European and Japanese beeswaxes depend on the species of the bees rather than on the floral origin of the honey.

2. In this research, the samples No. 1 and No. 2 were the genuine Japanese beeswaxes which were secreted by the Japanese bee (*Apis indica*, Fab., var. *Japonica*, "Rads," 1887), and the other six samples were produced by the European bees (*Apis mellifica*, L., 1761) and their cross-breeds.

3. It is important that the influence of the use of artificial comb should be borne in mind.

I wish to express my sincere thanks to Professor Seiichi Ueno for his kind guidance throughout this work, and also to Mr. Suekichi Suwa for the supply of the materials used in this research.

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A Method for the Determination of Small Quantities of Hydrogen Sulphide: the Determination of Sulphur in Small Samples of Steel.*

BY S. G. CLARKE, Ph.D., A.I.C.

IT occasionally happens that analyses of steels are required when the amount of sample available is too small for the ordinary processes of steel analysis to be of service. In certain cases, such as the study of segregation in steel, metallurgists are handicapped by lack of suitable methods for the analysis of small samples. This is more especially true in the determination of sulphur and phosphorus because of the very small percentages of these elements which are in question. The ordinary methods of determination call, at any rate in the case of sulphur, for a sample weight of 5 grms. of steel. For the purposes for which the method to be outlined was developed, the sample weight available for a determination was 0·1 grm.

There are two main methods for the determination of sulphur in steel: the gravimetric barium sulphate process, and the evolution process, which consists in dissolving the steel in a non-oxidising acid and determining the liberated hydrogen sulphide by a volumetric method, such as titration with iodine solution. The latter type of method is not so generally applicable to all kinds of steel as the former, but apart from certain alloy steels, *e.g.* those containing tungsten, molybdenum or copper, the evolution process is generally regarded as giving results which are quite as satisfactory as those from the gravimetric process, and it is, moreover, more rapid.

In view of the urgency of finding a method suitable for these small samples of steel it was decided to explore the possibilities of the evolution process, as being the most likely direction in which a workable process might be found. A process was worked out on the following lines:

* Communication from the Research Department, Woolwich.

OUTLINE OF THE PROCESS FOR STEEL.—By employing a special apparatus of simple design it is possible to dissolve the small sample of steel out of contact with the air in an atmosphere of hydrogen. It has been found that by using dilute sulphuric acid (1:3), which possesses advantages over other acids in the process to be described, the whole of the sulphur in the sample is evolved, and can be collected as sulphide in a small volume of dilute sodium hydroxide solution; it can then be readily determined by a new colorimetric method which depends on measuring the amount of iodine (in carbon tetrachloride solution) used in oxidising the sulphide in slightly acid solution.

COLORIMETRIC METHODS FOR DETERMINING HYDROGEN SULPHIDE.—In order, when working with a decigram sample of steel, to obtain results which would be of an order of accuracy comparable with that expected of the usual processes, the method employed would have to be reliable to within ± 3 thousandths of a milligram of sulphur on a total weight of under one-tenth of a milligram. An investigation of colorimetric processes available has revealed that they are valueless for the present purpose.

The conversion of dimethyl-*p*-phenylenediamine into a blue dye by hydrogen sulphide and ferric chloride has been found to possess the drawback that the colours produced are not strictly reproducible, nor are they due entirely to the reaction product of hydrogen sulphide; the reaction is, moreover, not nearly sensitive enough.

An experimental survey of metal sulphides as a basis for a colorimetric process for determining traces of hydrogen sulphide showed, at first, promising results as regards sensitiveness in the case of antimony and, in particular, lead. These methods, however, are quite empirical, since the depth and quality of the colour produced from a certain amount of hydrogen sulphide seem to be entirely dependent upon arbitrary conditions prevailing in the reaction solution. Attention has already been drawn (Evers, ANALYST, **1920, 45, 391**) to the influence of the *p*H value of the solution upon the intensity of the colour of the lead sulphide when used to determine lead; in the present case it has been found that, in alkaline solution, a colour is produced which is much darker than in dilute acetic acid solution. Attempts were made to obtain consistent results, working with a standardised solution of sodium sulphide (prepared in the manner indicated below) by controlling what variables could be controlled, *e.g.* the concentration of salts, acetic acid, the lead chloride added, the gum arabic protective colloid used, the temperature of the solution, etc., and by adhering to a rigid routine in the order of mixing reagents. Even in these circumstances the results were barely within the limits of accuracy desired, the colorimetric comparisons being carried out with the aid of a Klett colorimeter. No success could, however, be achieved in the application of this lead sulphide method to the determination of the sulphide disengaged from steel by acid and absorbed in alkali, largely owing to the practical difficulties in producing the colour under precisely the conditions prevailing in the preparation of a standard solution.

THE NEW COLORIMETRIC METHOD.—It is known that iodine can react quantitatively with hydrogen sulphide in aqueous solution, with the formation of sulphur and hydriodic acid, and this is the basis of a volumetric process commonly used for determining sulphide. If, however, the iodine consumed could be determined colorimetrically it might be expected that the reaction could be used for determining smaller amounts of sulphide than would be feasible in the volumetric method. A process on this basis would have the advantage of being an absolute one if the amount of sulphide could be calculated from the amount of iodine used.

It has been found that minute amounts of sulphide can be determined by shaking a slightly acid (sulphuric) solution containing the hydrogen sulphide in a closed flask with a known excess of iodine in carbon tetrachloride, and determining colorimetrically the residual amount of iodine by comparison with another known amount of iodine in carbon tetrachloride. Before applying this method to steel analysis it was tested upon a standardised sulphide solution. The following method was adopted:

A standardised sodium sulphide solution (approx. $N/200$) was run into a small flask of about 50 c.c. capacity, having a well-fitting glass stopper, 4 drops of dilute sulphuric acid (1:3) were added, standardised iodine in carbon tetrachloride (approx. $M/200$) was immediately run in, and the flask stoppered. It was shaken vigorously for about 20 seconds, an amount of carbon tetrachloride was added from a burette to bring the total volume of this liquid in the flask up to 10 c.c., and the contents of the flask were poured into one cup of a Klett colorimeter. Into the other cup was run a suitable volume of the standardised iodine solution, together with the amount of carbon tetrachloride, to bring the volume to 10 c.c. The ratio of the depths of the two solutions which transmitted the same amount of light was then found, the unused iodine being then readily calculated. Some results which were obtained are recorded in Table I.

The results show that the amount of iodine consumed for a certain weight of sulphide is independent of the initial excess of iodine used over the range examined. It may, therefore, be concluded that the same reaction occurs between iodine and hydrogen sulphide when these are shaken together in a mixture of carbon tetrachloride and water as when the organic liquid is absent, and that the amount of sulphide present can be calculated from the amount of iodine used according to the ordinary equation.

The sulphide solution used was prepared by passing about 50 c.c. of hydrogen sulphide into 250 c.c. of cold, freshly boiled water, to which a little sodium hydroxide had been added. The solution was standardised by adding a distinct excess of iodine (0·01 N) to a portion immediately after it had been acidified, allowing the mixture to stand for five minutes, and determining the excess of iodine with standardised very dilute thiosulphate solution, with starch as indicator. The solution of iodine in carbon tetrachloride was made and standardised as described later for use in the process for steel.

TABLE I.

Added.			Found.		
Sulphide solution. c.c.	Sulphide sulphur. Mgrm.	Iodine solution. c.c.	Iodine solution remaining. *c.c.	Iodine solution consumed. c.c.	Sulphur. Mgrm.
1·0 of 0·0048 *N*	0·077	2·0	$\frac{30}{27·0}\times 1·0=1·11$	0·89 of 0·0053 *N*	0·076
1·0 ,,	0·077	3·0	$\frac{15}{21·3}\times 3·0=2·11$	0·89 ,,	0·076
1·0 ,,	0·077	5·0	$\frac{30}{22·0}\times 3·0=4·08$	0·92 ,,	0·078
0·5 ,,	0·039	1·0	$\frac{30}{28·3}\times 0·5=0·53$	0·47 ,,	0·040
0·5 of 0·00635 *N*	0·051	1·0	†$\frac{25}{35·0}\times 0·5=0·36$	0·64 of 0·00533 *N*	0·055
0·5 ,,	0·051	2·0	$\frac{30}{21·5}\times 1·0=1·40$	0·60 ,,	0·051
0·5 ,,	0·051	3·0	$\frac{20}{16·9}\times 2·0=2·37$	0·63 ,,	0·054
1·0 ,,	0·102	3·0	$\frac{20}{22·3}\times 2·0=1·80$	1·20 ,,	0·102
1·0 ,,	0·102	5·0	$\frac{30}{15·8}\times 2·0=3·80$	1·20 ,,	0·102

* This column shows the ratios of the depths (in mm.) of the solutions used for comparison and the experimental solutions, when the field viewed in the colorimeter was uniform, multiplied by the number of c.c. of standard iodine solution contained in the 10 c.c. of comparison solution, giving the number of c.c. of standard iodine solution remaining after interaction with the sulphide.

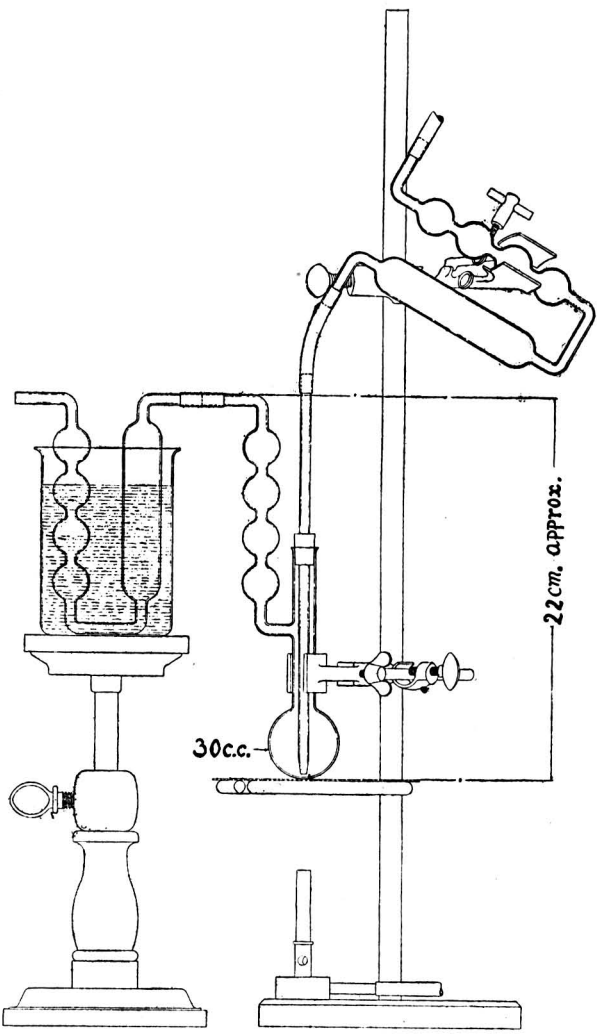
† Rather brownish colour of the experimental solution.

THE EVOLUTION OF HYDROGEN SULPHIDE FROM SMALL STEEL SAMPLES.—Preliminary experiments showed that it was not possible to obtain quantitative recovery of sulphur by treatment of the steel with acid unless this was done in an atmosphere of hydrogen. In order to avoid wastage of hydrogen, definite volumes were used from an approximately graduated aspirator; for the initial removal of air from the apparatus, 500 c.c. of hydrogen was found to be a safe amount, and a similar quantity was used for sweeping out after the steel had dissolved. It may be noted that the hydrogen used contained a fraction of one per cent. of oxygen, but, in view of the satisfactory results obtained, it would appear that this concentration of oxygen is not harmful. Before entering the apparatus the gas was passed through lead acetate solution and then through water.

The apparatus, which had to be designed for this work, and the construction of which is shown in the diagram, comprises the following parts:

(*a*) *The Evolution Flask.*—This is a flask of 30 c.c. capacity. It has a vertical side arm, carrying four bulbs, which has a two-fold function: (i) As a reflux condenser, preventing appreciable loss of water during the solution of the

steel; (ii) as a very efficient preventer of acid spray, charged with ferrous salt, being carried into the receiver. This apparatus can be readily made by cutting off the side tube from a Wurtz flask close to the join, and fusing on, in its place, the limb carrying the bulbs of a Mitscherlich absorption U-tube which has been



severed at the base. This flask is closed by a cork carrying a glass tube which reaches nearly to the bottom of the flask, and the lower end of which is somewhat constricted.

(*b*) *The Acid Container* is a Mitscherlich absorption tube in which the acid is placed at the outset. It is connected with the entry tube of the above flask by

about three inches of black rubber tubing, so that, after air has been removed from the apparatus by the passage of hydrogen, acid can be run on the steel merely by releasing the clamp and tilting the container.

(*c*) *The Absorption Tube* is another Mitscherlich absorption tube in which the small volume of dilute sodium hydroxide is placed; it is connected by black rubber tubing with the side arm of the evolution flask. The tube stands in a beaker of cold water supported as shown in the diagram.

(*d*) *The Bunsen Burner:*—This is a burner of the small type, such as is used for heating the mirror-tube in electrolytic arsenic determinations.

A number of different acids were tried, but the only one found suitable was dilute (1:3 by volume) sulphuric acid. Hydrochloric acid, even when more dilute than the constant-boiling mixture, gave rise to trouble, owing to irregular amounts of it passing over, and partly or wholly neutralising the necessarily small quantity of alkali in the absorption tube. Hydrobromic acid (1·49 sp. gr.) was found to be more satisfactory than hydrochloric acid by reason of its higher boiling point, but, nevertheless, a little found its way into the alkali; here it was found to interfere with the subsequent iodine colorimetric method for sulphide, owing to its causing a very marked reduction in the partition coefficient of iodine between carbon tetrachloride and the aqueous solution, and thereby causing loss of iodine.

METHOD FOR THE DETERMINATION OF SULPHUR IN STEEL.—The following method was adopted for the determination of sulphur in small samples of steel:

The sample of steel (0·1 grm.), in the form of fine drillings, is brushed into the flask, care being taken to prevent any particles sticking to the neck of the flask. Dilute sodium hydroxide solution (2 c.c. of a 10 per cent. solution) is run from a pipette into the Mitscherlich absorption tube, the addition being made to the limb carrying the bulbs. Dilute sulphuric acid (5 c.c., 1:3) is similarly run into the upper Mitscherlich tube, which acts as the acid container. The whole apparatus is now assembled, and the acid container adjusted to such an angle to the vertical that gas can pass freely through it without passing through the volume of acid which it contains.

Hydrogen is passed in a rapid stream through the apparatus for 1 to 2 minutes, approximately 500 c.c. being used. The rate of supply of hydrogen is then reduced to a flow of about 2 to 3 bubbles per second. The acid container is removed from its clamp and tilted so that the acid runs into the flask, and immediately it has done so the container is replaced in the clamp and the burner lighted under the flask, the liquid in which is rapidly heated to boiling. The flame is then reduced to maintain only a steady boiling, when, with fine drillings of medium carbon steels, complete solution of the sample (with the exception of a little carbonaceous matter) will take place in less than two minutes.

When the steel has dissolved, the rate of flow of hydrogen through the apparatus is again increased to that used in the initial sweeping out, and about the

same quantity allowed to pass.* The flame is then extinguished, the hydrogen supply stopped, the rubber tube joining the acid container to the leading tube to the flask is disconnected, to prevent sucking back, and the absorption tube is detached.

The liquid in the absorption tube is poured (from the limb which was attached to the flask) into a small flask which has a *well-fitting* glass stopper (a 50 c.c. volumetric flask was used); about an equal volume of water is used for rinsing out the absorption tube, the rinsings being added to the main volume in the flask.

One c.c. of dilute sulphuric acid (1:3) is added, and the flask is placed in cold water and moved about gently therein for about half a minute in order to cool after the neutralisation of the alkali. Without delay exactly 2 c.c.† of the standard solution of iodine in carbon tetrachloride is run into the flask from a small accurate 10 c.c. burette, and the stopper immediately inserted.

The flask is now shaken vigorously for about 30 seconds. Exactly 8 c.c. of carbon tetrachloride (or 9 c.c. if only 1 c.c. of the standard solution had been used) is then run into the flask; the contents are mixed and poured into the cup of a Klett colorimeter, no rinsing of the flask being necessary.

COLORIMETRIC COMPARISON.—One c.c. of the standard iodine solution is run into the other colorimetric cup, 9 c.c. of carbon tetrachloride are added, and the solution mixed (0·5 c.c. and 9·5 c.c. of iodine solution and carbon tetrachloride, respectively, are taken when only 1 c.c. of iodine was used in the above method). The colorimeter having previously been adjusted as regards zero points and equality of lighting of the tubes, the depth of the sample solution required to balance any particular depth of the above comparison solution is measured.

The iodine remaining (as c.c. of standard solution), after reaction with the hydrogen sulphide, is simply

$$\frac{x}{y} \times n$$

where x = depth (in mm.) of the comparison solution,

y = depth (in mm.) of the sample solution,

n = c.c. of standard iodine solution (generally 1) added to the comparison tube.

* During the experimental work a second absorption tube, containing an alkaline lead solution, was connected with the main alkali absorption tube shown in the diagram. Absorption of the hydrogen sulphide by the alkali in the first tube was thereby shown to be complete, in spite of the very rapid flow of hydrogen used in the sweeping out, because the same alkaline lead absorption tube was used each time and no darkening of the solution could be detected at the time of completion of the work.

† Or 1 c.c. when the sulphur content of the steel is known definitely to be low, say, less than 0·03 per cent. This gives a little greater accuracy in the colorimetric determination with steels low in sulphur, but 2 c.c. would serve quite well for all steels up to 0·08 per cent.

The value of y taken should be the mean of several readings, and the ratio $\frac{x}{y}$ should agree closely with a fresh ratio obtained by using a different value for x.

The amount of standard iodine solution used in the reaction with the hydrogen sulphide is obtained by deducting the above value from the amount originally used, whence the amount of sulphur can be readily calculated from the strength of the iodine solution employed:

1 c.c. of $N/200$ iodine = 0·080 mgrm. of sulphur.

THE STANDARD IODINE SOLUTION.—This is prepared by dissolving 0·32 grm. of iodine in carbon tetrachloride; this can be carried out rapidly by covering the iodine with carbon tetrachloride, warming on a steam bath until an opaque solution is obtained, and then treating the remaining iodine with fresh portions of the solvent until all is dissolved. The cooled solution is diluted to 500 c.c. It is standardised by titration with arsenious acid ($N/100$) as follows:—Twenty c.c. of the iodine solution are run into a 500 c.c. flask, and 100 c.c. of water and 20 c.c. of dilute (5 per cent.) potassium iodide are added, followed by a few grms. of sodium bicarbonate. About 9 c.c. of the arsenic solution are added, the solution is well shaken, and the titration finished, after the addition of starch solution, up to the practical disappearance of the blue colour; very vigorous shaking is necessary near the end-point. The addition of potassium iodide is necessary to reduce the partition coefficient of iodine between carbon tetrachloride and water.

IMPORTANT POINTS IN THE PROCESS.—(*a*) Steels which are low in carbon, and contain a relatively small percentage of impurities, generally dissolve much more slowly in acid than ordinary steels. This is the case, *e.g.* with British Chemical Standard "A_2" steel (S, 0·020; C, 0·037), and results for sulphur first obtained with such steel by this method were too high; this was traced to the fact that the acid had become concentrated by evaporation during the dissolving process, and the presumption was that traces of a reducing gas, other than hydrogen sulphide, thereby became liberated; a crystalline precipitate (ferrous sulphate) was noticed in the flask in the experiments in which high results were obtained. Good results were obtained with such steels when the flame under the flask was turned very low during the dissolving of the steel, so as to avoid undue concentration of the acid. The formation of crystals in the flask, before it cools down after an experiment, is to be regarded as an indication of danger.

(*b*) The standard comparison solution in a colorimeter cup will alter appreciably in iodine concentration if kept for, say, more than 15 minutes, because carbon tetrachloride is a somewhat volatile liquid. Incorrect results will then be obtained in the determination of the iodine remaining after interaction with hydrogen sulphide, since this solution does not lose carbon tetrachloride at the same rate as the comparison solution, owing to its being covered with a layer of water.

Table II contains results obtained in the process with British Chemical Standard steels.

TABLE II.

Steel.	Weight taken. Grm.	Iodine solution.* c.c.	Iodine solution† remaining after reaction. c.c.	Iodine solution consumed. c.c.	Sulphur found. Per Cent.	Mean certificate result. Gravimetric.	Mean certificate result. Volumetric.
Blank—no steel		1·0	$\frac{30·0}{30·0}\times 1·0=1·0$	nil			
A_2	0·1	1·0	$\frac{30·0}{38·0}\times 1·0=0·79$	0·21	0·019	0·020	0·021
,,	0·2	2·0	$\frac{30·0}{19·0}\times 1·0=1·58$	0·42	0·018		
O_1	0·1	1·0	$\frac{25·5}{20·0}\times 0·5=0·64$	0·36	0·031	0·032	0·032
	0·2	2·0	$\frac{30·0}{23·0}\times 1·0=1·30$	0·70	0·030		
H_1	0·1	2·0	$\frac{30·0}{19·5}\times 1·0=1·54$	0·46	0·039	0·041	0·042
	0·1	1·0	$\frac{30·0}{29·5}\times 0·5=0·51$	0·49	0·042		
	0·2	2·0	$\frac{30·0}{30·4}\times 1·0=0·99$	1·01	0·043		
N_1	0·2	3·0	$\frac{20·0}{22·0}\times 2·0=1·82$	1·18	0·050	0·050	0·051
V‡	0·1	2·0	$\frac{30·0}{23·2}\times 1·0=1·29$	0·71	0·060	0·063	0·062
P	0·1	2·0	$\frac{30·0}{26·3}\times 1·0=1·14$	0·86	0·073	0·073	0·073

* 0·00530 N; 1 c.c. = 0·085 mgrm. of sulphur.

† This column has the same significance as in Table I.

‡ Chromium-vanadium steel: V., 0·27 per cent.; Cr, 0·86 per cent.

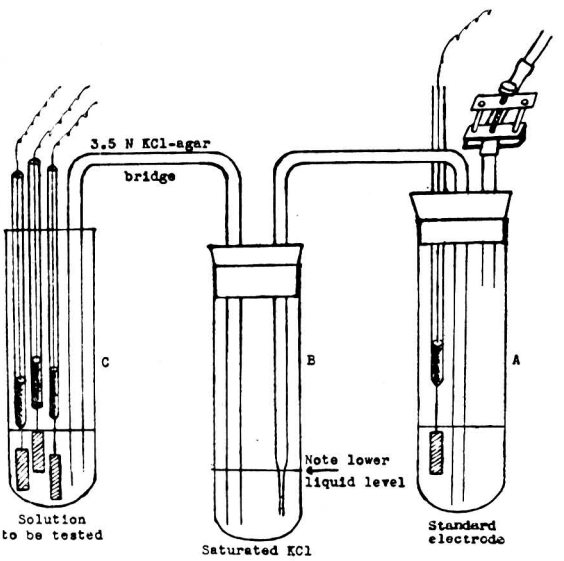
The results obtained by working with different quantities of sample (0·1 grm. and 0·2 grm.) show satisfactory agreement.

The Use of the Quinhydrone Electrode.

By GEORGE M. MOIR, Ph.D., F.I.C.

(*Pedler Research Scholar of the Institute of Chemistry.*)

The determination of the *p*H value, by means of the hydrogen electrode, is a slow process owing to the fact that the gas must be passed through the liquid for about 5 to 10 minutes before a reading can be taken, and then the electrode must be cleaned and boiled before being ready for another determination. The quinhydrone electrode introduced by Biilmann permits determinations of *p*H on the acid side to be carried out very much more rapidly. For many purposes it is



distinctly more accurate than colorimetric methods, and is scarcely less rapid. The reliability of any method of determining *p*H is, however, governed by the nature of the solution being investigated, and cases are known in which even the hydrogen method must give place to the colorimetric procedure. The quinhydrone electrode has the special advantage that it can be used according to the method of Knudsen (*Z. Unters. Lebensm.*, 1925, **50**, 300), for solid or semi-solid material, such as cheese or gelatin, etc.

Instead of the usual type of standard electrode vessel to which is fused a side-tube, I have devised a simple arrangement consisting of an ordinary test-tube of stout glass, about 1″ × 4″, fitted with a rubber stopper in which three holes are bored (A, Fig. 1). Through these holes pass, respectively, the glass tube of the

electrode, an inverted U-tube, the outer end of which ends in a capillary, and a third short tube with rubber tube and screw clip attached; if necessary, the apparatus can be made air-tight by applying a trace of vaseline to the cork. This apparatus has three advantages: first, it is inexpensive, and any breakages can be easily and rapidly replaced; second, it is flexible, for the U-tube can be rotated to any required position; third, it can be readily slipped into a metal rack in a water-bath or thermostat. The diagram shows how connection is made with the solution to be tested, which is usually placed in another short test-tube (C) standing in the metal rack. The intermediate tube (B), which contains saturated potassium chloride solution, is usually put outside the water-bath. It is fitted with a cork having large holes, or slots cut in the side, so that the tubes can be easily slipped in and out.

The actual electrode in A may be of bright platinum, since it is always in contact with the same solution, and is not so liable to "poisoning"; but if difficulties are encountered, a gold one may be found better. The electrodes for use in the solution to be tested are preferably made of gold foil (about $1{\cdot}0 \times 0{\cdot}5 \times 0{\cdot}025$ cm.), to which gold wire (S.W. Gauge 21) is attached, first by hammering, and then by heating just to redness. By the same method the gold wire is then attached to a platinum wire to be fused into a glass tube. Some workers use gold-plated platinum electrodes on account of the risk of melting the gold during flaming, but this gold plating requires renewing from time to time. All-gold electrodes can be flamed without difficulty, provided this is done at a distance from the bright light of a window, so that care can be taken not to heat beyond the first sign of redness. The flaming must be done with an alcohol lamp, to avoid the risk of "poisoning" by coal-gas impurities.

The frequent flaming may cause cracks to develop in the tube into which the platinum wire is fused. Care should be taken to obtain suitable glass tubing for this purpose, in order to avoid loss of time due to frequent cracking; in fact, the process of fusing the platinum properly into tubes—simple as it appears—may very well be delegated to an expert. Abnormal potentials are sometimes caused by leakage of liquid through cracks, which I have found to be most readily detected by keeping the electrodes, when not in use, in a test-tube with strong nitric acid. This gradually passes through the crack and attacks the mercury within, producing a white salt. The mercury used to put in these tubes ought to be clean, pure, and dry, and is best kept in a bottle fitted with dropping-tube and rubber teat, so that small quantities can be transferred without loss.

If by accident an electrode becomes amalgamated, the mercury can be removed by flaming, but on occasion blackish deposits remain—probably due to copper which may have reached the mercury from a connecting wire. These deposits can be removed by plunging the electrode while almost red-hot into strong nitric acid. Scrubbing with a clean brush and soap and water has been recommended for removing sticky material from the electrodes prior to flaming. Another method is to place the electrode in a tube with nitric or chromic acid

set in a boiling water-bath, and sometimes it may be necessary to use all these methods repeatedly. In other cases, failure to give correct results is due to the mercury in the tube becoming moist (especially with acid fumes), whereby a small mercury-copper cell results and causes an abnormal potential.

Connection between B and C is made by means of an agar bridge, which is prepared by adding 5 grms. of agar-agar to 100 ml. of 3·5 *N* potassium chloride solution, and heating in a large test-tube (or beaker) immersed in boiling water. Several U-tubes of suitable size are prepared, clean and dry. To one end of each is fitted a piece of rubber tubing and clip, so that it can be filled by suction, and the clip applied when full. The other end must be left in the test-tube until the whole mass is quite solid, when it may be removed, and, after detaching the rubber tube, it should be kept until required with both ends in test-tubes of saturated potassium chloride solution. Before using, the end which is to go in the solution to be tested should be left for ten minutes in distilled water and rinsed clean. This is of importance, because very small quantities of potassium chloride are able to cause considerable reductions in the *p*H value. The advantage of an agar bridge is that it minimises the risk of potassium chloride reaching the solution to be tested. In fact, it is possible that some of the slight differences which Lester (*J. Agric. Sci.*, **14**, 634) found between the quinhydrone and the hydrogen electrode may have been due to this cause. Biilmann (*Trans. 2nd Comm. Intern. Soc. Soil. Sci.*, 1927, B, 236) has drawn attention to the risk of siphoning occurring, and for this reason the liquid level in B should be distinctly lower than that in either of the other two tubes.

The difficulties associated with the preparation of a standard calomel electrode for reference purposes can be avoided by the use of a solution containing potassium chloride (0·09 *N*) and hydrochloric acid (0·01 *N*) in the presence of undissolved quinhydrone. Although Veibel (*J. Chem. Soc.*, 1923, **123**, 2203) found that the potential of this mixture remained constant for several days, it is preferable to renew it daily. The vessel A should be rinsed once or twice with small quantities of this solution, which are blown out through the U-tube. It is then filled about half full, and a small amount of quinhydrone added (0·1 grm. is usually sufficient). After replacing the cork, the U-tube is filled by blowing gently, and the clip at once closed. Air bubbles above the capillary greatly reduce the sensitiveness of the apparatus. If the cork fits well, little or no leakage should take place from the capillary. After using the apparatus, A should be disconnected from B if no further measurements are to be made for a few hours. Immediately after disconnecting, the clip on A should be opened slightly and a few drops allowed to run out of the capillary, so that any strong potassium chloride solution which may have diffused in will not be allowed to flow back into the apparatus. This precaution is essential if the reference electrode is to be maintained correct for more than one day.

I have found one electrode in A sufficient, but Lester's plan of having three in the solution to be tested was adopted. Thus, when one became "poisoned" it

was at once observed because it gave a different reading from the others. "Poisoning" did not often occur when dealing with clear solutions, but liquids like milk, especially after the protein had been coagulated, gave more trouble. In such cases, washing the electrodes, first under the tap, and then with distilled water, did not suffice, but, in addition, flaming was often necessary after each determination. In order to obtain good results in solutions or mixtures containing clotted material, it may be necessary to use a larger vessel for C and to stir the liquid mechanically, as Lester did.

Every day before measuring an unknown *p*H a solution of known *p*H should always be tested. For this purpose, 0·05 *N* potassium phthalate, which has a *p*H of 3·97, is convenient. "Standard acetate" mixture, which is 0·1 *N* with respect to both acetic acid and sodium acetate, and which has a *p*H of 4·626, is easily made up from standard acid and sodium hydroxide solutions of about half-normal strength. A few ml. of the solution to be investigated are placed in C (which need not be quite dry except for highly accurate measurements), the agar bridge inserted, and about 0·1 grm. of quinhydrone added with a spatula. The electrodes are at once inserted and used to stir the mixture briskly, and the potentiometer reading taken as soon as possible (because of the fact that a drift takes place after a time in certain solutions). When the value obtained for a solution of known *p*H differs by more than a millivolt from what is expected, an investigation and cleaning of the apparatus and solution should be carried out. The formula for calculating the *p*H when using the reference electrode described above is:

$$p\mathrm{H} = 2{\cdot}03 + \frac{\mathrm{E}}{0{\cdot}0577 + 0{\cdot}0002(t - 18)}$$

where E is the voltage (in volts) and $t°$ C. is the temperature. By drawing a graph of *p*H against E.M.F. at 18° C. the *p*H values can be read off at a glance. Lines can be drawn to obtain the values at adjacent temperatures.

The statement is generally made that the availability of the quinhydrone electrode is confined to the acid side, but Biilmann himself has compared it with the hydrogen electrode, and obtained results agreeing well, even at *p*H values above 7·0. Lava and Hizon (*Chem. Abst.*, 1929, **23**, 538) found it satisfactory up to *p*H 9·0, provided that the potentiometer readings were taken promptly after adding the quinhydrone. I have not come across records of trials with it at higher *p*H values.

Many workers have published results which they have obtained by means of the quinhydrone electrode (*cf.* Watson, *Ind. Eng. Chem.*, 1927, **19**, 1272), but I have found the papers cited in the references especially useful. A number of important details given above have been taken from Biilmann's paper, which may not be so readily available as others.

NATIONAL INSTITUTE OF RESEARCH IN DAIRYING,
UNIVERSITY OF READING.

A Simple, Inexpensive Quinhydrone Cell for Rapid Work.

By J. G. DAVIS.

Moir has described a modified quinhydrone electrode (preceding paper). The apparatus now described is a further simplification, and was prepared for determining the *p*H of a large number of samples of liquid or solid substances without the aid of salt-agar bridges or glass taps.

The half cell consists of a pyrex tube, about $\frac{1}{2}$ inch in diameter, which has been drawn out into a fine jet and bent over as shown in Fig. 1. It is important that

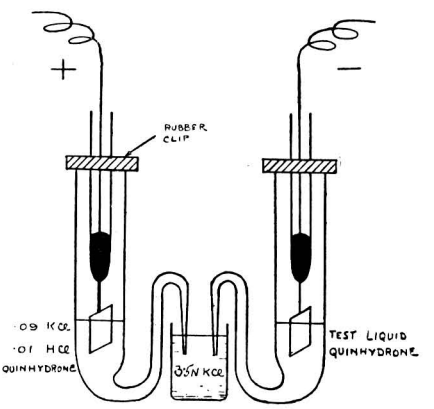


Fig 1

the jet be about $\frac{3}{4}$ to 1 inch above the bottom of the tube. To prepare the standard quinhydrone half cell, pour some hydrochloric acid potassium chloride reagent (9 parts of 0·1 *N* KCl and 1 part of 0·1 *N* HCl, very accurately standardised) into the cell, add about 0·05 grm. of quinhydrone, shake, allow to settle, and then gently blow over. No bubbles should be allowed in any part of the cell. The amount of liquid put in should be so gauged that when blown over, the level is about $\frac{1}{4}$ inch above the jet, thus preventing siphonage. For *p*H determinations of liquids a similar cell is prepared, except that the liquid under test is used instead of the hydrochloric acid–potassium chloride solution.

Gold electrodes, after having been rinsed in distilled water and flamed to a dull red heat (momentarily) in a pure alcohol flame, are immersed in the cells, the jets of which are dipped into 3·5 *N* potassium chloride solution just before a reading is taken and removed immediately afterwards.

Sensitivity is good, and a constant value should be obtained in 2 to 3 minutes from the time of mixing-in the quinhydrone. For solids, either of two methods may be used:

(1) The solid is ground in a mortar with quinhydrone, pressed into a short piece of tubing (a one-inch section of a test tube $\frac{1}{2}$ inch in diameter), and the electrode inserted in this "mush," which is then allowed to dip into saturated KCl and contact made as before (Fig. II.).

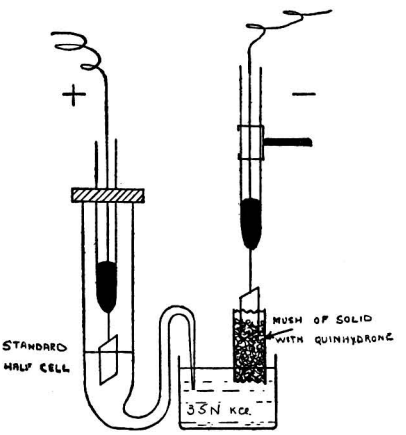


Fig II

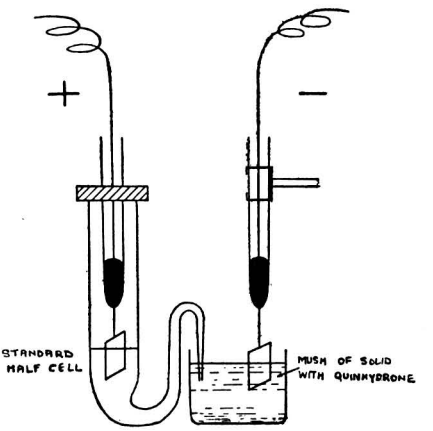


Fig III

(2) The jet of the standard half cell is allowed to touch the "mush" in a crucible about 1 inch from the electrode. No appreciable error was detected when using well-buffered solids over a range of *p*H from 3 to 7 (Fig. III).

The cells may be emptied by jerking the liquid out and then blowing back *through* the jet.

The half cells can be obtained from Mr. W. J. Nelson, 77, Streatham Vale, S.W.16; price 1s. 6d. each.

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Notes.

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

OSMIUM TETROXIDE POISONING.

I HAVE been unable to find any record of fatal cases due to exposure to the fumes of osmium tetroxide, but indirectly one case of fatal poisoning has come to my notice. This case was referred to by Mr. C. M. Hoke in an article appearing in the *Jewelers' Circular*. My interest lies particularly in determining the pathology both of the acute condition and of chronic poisoning, with the expectation of subsequently developing some method of neutralising the effects.

It may not be generally known that inhaling the fumes of osmium tetroxide in high concentration is a very dangerous procedure; and, if the effect on human beings is at all analogous to that on experimental animals, it would seem probable that some cases of fatal poisoning must have occurred in the past. In animals, at least, the cause of death is a pneumonia which appears very shortly after their exposure to the fumes.

Any information that can be given me in this connection will be deeply appreciated.

F. R. BRUNOT.

U.S. PUBLIC HEALTH SERVICE,
WASHINGTON, U.S.A.

THE POSSIBLE EFFECT OF SULPHUR DIOXIDE WHEN USED AS A PRESERVATIVE FOR DRIED FRUITS, ETC.

IN the course of routine work on products preserved with sulphur dioxide, and more particularly with fruit juices, the presence of hydrogen sulphide has made itself evident to the users by its odour and the flavour of the juices after dilution.

Under some conditions the presence of hydrogen sulphide was suspected in dried fruits also, and it was in connection with the examination of some hundreds of such samples that the following information was gathered.

For the prevention of the growth of moulds and the elimination of living organisms, it is necessary to "sulphur" such fruits as raisins, sultanas, apricots, peaches, apples and pears before they are marketed, and, for the preservation of fruit juices, either sulphur dioxide or benzoic acid may be employed.

In the course of work undertaken in Spain, France, Italy and Greece, I have been able to reduce the proportions of sulphur dioxide to a minimum without diminishing the market value or keeping qualities of the dried fruits, but the moist pulps need different treatment, and the existing Regulations permit the use of larger proportions. It is in these products, which are used for the preparations of syrups and "soft" drinks, that the effect of sulphur dioxide is most pronounced.

In order to demonstrate the possible state or situation of the sulphur dioxide in dried fruits, the following examination was made of a shipment of sultanas:

Sulphur dioxide before washing	..	375 parts per million.
,, ,, after washing	..	320 ,, ,, ,,
,, ,, in the washings	..	45 ,, ,, ,,

This seems to indicate plainly that most of the gas is present as an actual compound of the aldoses with the sulphite.

It might be argued that such a compound was entirely harmless to consumers of such fruit, but such a contention would not hold good if the dried fruit were used for making, say, artificial wines, mince meat or sauces, and the same disability is attached to the use of fruit pulps containing sulphite, either added purposely or left in barrels accidentally after cleaning, for I have found that a yeast fermentation becomes possible in diluted solutions; and, when that is active, the sulphur compounds are reduced to hydrogen sulphide.

To prove that this was possible, I expressed the juice from some Almeria grapes, sterilised it by boiling, and divided it up in flasks. To one, sulphur dioxide was added in the form of sodium bisulphite to approximately the proportion of 750 parts per million, as permitted in the Regulations. To another nothing was added. Both were then inoculated with a platinum wire dipped in an active growth of yeast. Other flasks were used as controls, and the neck of each was covered with a piece of lead paper and an inverted beaker.

After 24 hours at 65° F. an active fermentation was set up in the plain juice, but nothing had commenced in those containing sulphur dioxide. These were then diluted with more sterilised juice and left for several days under the same conditions, the results being as follows:

Flasks, to which no sulphur dioxide had been added, produced no coloration whatever on the lead paper, but with those containing the diminished proportion of sulphur dioxide, active fermentation had started, and the lead papers were marked with a perfectly defined black disc on an unstained white background.

Some difficulty was experienced in obtaining dried fruit free from sulphur dioxide for similar tests, but such samples as I have tested and found free from it yield no blackening whatever with lead paper when they are suitably mixed with water and fermented.

A fermentation test for the presence of sulphur dioxide, is too complicated for routine work, but I found that "sulphured" fruit and "sulphited" pulps have the disability that, when moistened or diluted with syrup, they develop an objectionable amount of hydrogen sulphide if once fermentation by yeast is allowed to commence.

It is necessary, therefore, to prevent the possibility of conditions which will permit fermentation, and, among other precautions, such products should be examined for the presence of active yeast cells; and if such are found present, the syrups or mixtures should be pasteurised before bottling.

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THE DETERMINATION OF PHOSPHORUS IN STEEL, ALLOY STEELS AND CAST IRON.

MR. ETHERIDGE, in his paper on "The Determination of Phosphorus in Steel, etc." (ANALYST, 1931, 14), begins by remarking that "Phosphorus is oxidised to orthophosphoric acid in nitric acid solution," and on page 16 he remarks that "oxidation

with permanganate is necessary to destroy organic matter. . . . The omission of permanganate leads to low results, possibly due to the interference of organic substances. . . ."

My own experience has led me to confirm the experience of others, that phosphorus is not completely oxidised to orthophosphoric acid when steel or iron is dissolved in *dilute* nitric acid, and that the addition of potassium permanganate is made for the main purpose of converting the phosphorus into orthophosphoric acid; the oxidation of carbonaceous matter is of decidedly secondary importance. Carbonaceous matter may be oxidised by means of several other oxidising agents, but very few of them will convert the phosphorus into orthophosphoric acid.

If a mild steel with very little carbon, but, say, 0·1 per cent. of phosphorus, is dissolved in dilute nitric acid, it will be found that, although there is little or no carbonaceous matter present, the precipitation of the phosphorus will be seriously low without the addition of permanganate, thus illustrating my point that the function of the permanganate is primarily to convert the phosphorus into orthophosphate. It may be mentioned, however, that if a steel is dissolved in dilute nitric acid or *aqua regia*, the complete conversion of the phosphorus into orthophosphoric acid will take place if the solution is evaporated and the residue baked.

Another interesting fact is that, so far back as 1885, J. Mackintosh showed that phosphorus in a solution of steel in hydrochloric acid may be oxidised to orthophosphoric acid by means of a stream of sulphur dioxide gas without oxidising the ferrous iron.

On page 16, Mr. Etheridge remarks that "it would be possible to add ammonium nitrate at this stage, but this would require less nitric acid to be used in dissolving the steel, which would be undesirable for rapid solution and oxidation of the carbides formed." He may be interested to know that in the "Analoid" method for phosphorus in steel, 2 grms. of drillings are dissolved in no more than 30 c.c. of nitric acid (sp. gr. 1·20), that solution takes place very quickly, and there is no difficulty with regard to oxidation of the carbides formed. Thousands of tests which have been made by works' chemists by this method over a period of ten years or so, support this statement.

On page 18, the author refers to my paper on the effect of titanium on the determination of phosphorus, but goes on to say that "It is fortunate that it is not usual to encounter low-phosphorus iron with much more than 0·01 per cent. of titanium." If, however, he refers to p. 111 of *The Proceedings of The Cleveland Institution of Engineers*, 1919–20, he will see that I have analysed 16 definite brands of pig iron from different parts of Great Britain, and that the titanium in these ranged from 0·08 to 0·42 per cent., the average being about 0·15 per cent. One feature of my paper was to show that most haematite pig irons contain a moderate amount of titanium, which calls for attention in the determination of phosphorus.

On p. 20, the author refers to vanadium and tungsten steels, and states that in tool steels with 15 per cent. of tungsten some of the tungsten is precipitated, and that this always carries down some phosphorus. It may be mentioned, however, that in a process which I have worked out, good results are obtained by dissolving the steel in nitric acid, followed by a liberal supply of potassium permanganate. This method, which has been in use for some ten years, was given in detail in the *J. Iron & Steel Inst.* (1926, No. 1, p. 464).

The reference to Messrs. Rooney & Clarke's paper, given on page 21 of THE ANALYST, contains a misprint—the year should be 1926, not 1925.

Taken as a whole, however, Mr. Etheridge's paper contains much useful information, and these remarks are not intended in any way to detract from its value.

N. D. RIDSDALE.

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WITH reference to Mr. Ridsdale's remarks on the use of potassium permanganate, while there is no doubt that low results are obtained if it is not used, the mechanism of its action is not clear. Most authorities consider that meta-phosphoric acid is formed, and that potassium permanganate assists in transforming this into ortho-phosphoric acid. In both acids the phosphorus is fully oxidised, and the transformation of meta-acid into ortho-acid is a hydration effect, not oxidation, hence the difficulty of explaining why permanganate is necessary. According to the text-books meta-phosphoric acid is quickly transformed into ortho-phosphoric acid by boiling in the presence of mineral acids, but this is retarded by organic acids. It is possible, therefore, that the permanganate, by destroying these acids formed from the carbon of the steel, may thus indirectly assist in the transformation of meta- to ortho-acid.

Dr. B. S. Evans has recently carried out some experiments which appear to show that phosphorous acid is formed on dissolving steel in nitric acid, and he has further found that dilute nitric acid has practically no oxidising action on phosphorous acid. Bauer and Deiss (*Sampling and Analysis of Iron and Steel*) also state that phosphorous acid is formed. Brearley and Ibbotson (*Analysis of Steel Works' Materials*) state that phosphorus in steel is not completely oxidised by nitric acid alone. It seems probable that phosphorous acid is formed in the first place and partly oxidised to phosphoric acid by oxides of nitrogen produced by dissolving the steel in nitric acid, but it is necessary to complete the conversion to phosphoric acid with an energetic oxidiser such as potassium permanganate. Dr. Evans has also shown that chromic acid is not a sufficiently powerful oxidiser in this case, having little or no action on phosphorous acid.

As regards the use of a smaller amount of nitric acid than is specified in the paper, while 30 c.c. would be satisfactory in many cases, there are alloy steels which deposit carbides which are difficult to dissipate, and for these an excess of nitric acid is an advantage.

My experience with haematite cast iron is, no doubt, considerably less than Mr. Ridsdale's, but I have not encountered any with more than traces of titanium.

With regard to Mr. Ridsdale's method for high tungsten steels, in which tungsten is held in solution by using less nitric acid throughout, it is admitted that tungstic acid is liable to separate, to some extent, in the later stages, and phosphorus must be recovered from this precipitate, as was pointed out by Rooney and Clarke (*J. Iron and Steel Inst.*, No. I, p. 466). Furthermore, the lower acidity favours co-precipitation of arsenic, which may demand a reprecipitation. Also, it is by no means safe to use the same values for the volumetric solutions unless they are standardised under the same conditions, as the precipitate of ammonium phosphomolybdate does not appear to be quite in accordance with the formula when precipitated from solutions containing only a small excess of nitric acid.

I wish to thank Mr. Ridsdale for his interesting comments.

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Notes from the Reports of Public Analysts.

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

COUNTY OF LANCASTER.

Annual Report of the County Analyst for the year 1930.

Of the 5303 samples examined, 4987 were taken under the Food and Drugs Act, and of these, 128 were adulterated. In the County of Lancaster it is now the general practice to take formal samples of milk and informal samples of other articles. If the informal sample is suspicious or adulterated a formal sample is taken from the same source.

Freezing-point Test of Milk.—Most of the milks received during the year which were deficient in solids-not-fat were submitted to this test in cases where it was possible to obtain an "appeal-to-cow" sample. The corresponding results in 32 cases (given in tabular form) show that the information obtained by the freezing-point test was identical with that gained from comparison with the corresponding "appeal-to-cow" sample.

Day-to-day Variation in the Milk of Two Herds.—A daily examination was made of the milk from a large herd and from a small herd at the Lancashire County Council Farm at Hutton, near Preston. The larger herd, which was sampled from July 5th, 1926, to November 15th, 1926, consisted of 39–45 cows, all non-pedigree shorthorns. The smaller herd, which also consisted of non-pedigree shorthorns, was sampled from September 24th to November 14th, 1928. It consisted of 11–14 cows.

The total solids were determined by weighing, often in duplicate. The fat was determined by duplicate Leffmann and Beam determinations in all cases; four determinations were carried out in all, if the first two did not agree. The refraction readings were obtained by the copper sulphate serum method (Analyst, 1927, **52**, 193) with the Zeiss immersion refractometer at 20° C. The specific gravity was determined, and in each case the calculated solids agreed well with the experimental figure.

Although the series taken from the larger herd extended from the hot weather of July to the cold weather of November, it will be observed that the solids-not-fat were practically constant throughout the whole of this time, whilst the variations in fat were unimportant. The results are given in full in tables in the Report.

Faced Pearl Barley.—An informal sample of pearl barley was found to be faced with maize starch to the extent of 1·3 per cent. A subsequent formal sample was similarly faced to the extent of 1·5 per cent., and the manufacturers were cautioned. Another sample faced to the extent of 0·2 per cent. with maize starch was also returned as adulterated.

Chalk in Ground Ginger.—Of the 98 samples examined, 2 were returned as adulterated. One of these contained 7·86 per cent. of total ash, 4·92 per cent. of ash insoluble in water, and 0·28 per cent. of sand. The insoluble ash consisted

largely of chalk, which is said to be added to prevent the growth of weevils.. Most of the ground ginger of commerce is free from added chalk, and, therefore, it would appear that this addition is not necessary. It may be alleged that some types of ginger are more prone to the attacks of weevils than others; but in this case it would appear desirable to inform the purchaser of the particular type of ginger supplied, and the necessity for such treatment, as some purchasers might prefer to avoid weevils by purchasing the type immune from their attack.•

JAM.—During the five years ended 1930, the number of samples of jam examined was 243, of which 12 were returned as adulterated. Eight contained foreign fruit, three contained glucose syrup when the label claimed that the jam was prepared from fresh fruit and pure sugar, and one contained excessive sulphur dioxide.

Many of the samples have been examined for their optical rotation, both before and after inversion, in 10 per cent. aqueous solution in a 200 mm. tube. The direct reading with mercury green light has varied between +6·55° and +0·11°, and the invert reading between −0·30° and −3·56°. The percentage of total sugars, as given by the refractometer, has varied between 58 per cent. and 74 per cent. In certain cases the amount of insoluble solids has been determined. The following are some of the results which have been obtained with single fruit jams:

Insoluble Solids in Jams. Per cent.

	Number.	Average.	Highest.	Lowest.
Blackcurrant ..	10	2·15	2·98	1·29
Strawberry ..	20	1·31	2·28	0·59
Raspberry	11	1·85	2·60	0·72
Apricot	4	1·25	2·76	0·68
Damson*	13	0·88	1·73	0·49

* Without stones.

POLISHED RICE.—Since the year 1926, 195 samples of rice have been examined in the County Laboratory, of which 16 have been coated with varying amounts of talc. Of these 16 samples, only three have contained more than 0·5 per cent. Some years ago it was by no means unusual for rice to be polished with talc, but in more recent years, as shown by the figures above, this practice has almost entirely ceased. This proves that it is unnecessary. The suggested limit of 0·5 per cent. made to the Local Government Board is most certainly too high; in fact there are many reasons why the use of talc should be entirely prohibited. It has been alleged that the facing of rice and other cereals is intended to prevent the attacks of weevils. It is very doubtful whether facing is of any value to prevent such attacks, and the fact that most of the rice now sold is free from such facing shows that the bulk of manufacturers find it to be unnecessary. The uncoated samples contained from 0·19 to 0·42 per cent. of ash.

G. D. ELSDON.

General Medical Council.

PHARMACOPOEIA COMMISSION.

REPORT OF THE COD-LIVER OIL COLOUR TEST SUB-COMMITTEE.*

SEVERAL modifications of the details of the antimony trichloride test, first proposed by Carr and Price, have been proposed from time to time, but no attempt has been made to show that even by adherence to any one form of the test, the same results are yielded in the hands of different workers. The Sub-Committee set out to determine this and to decide the conditions best calculated to give uniform results. It was found at the outset that when different members of the Sub-Committee examined the same samples of cod-liver oil, their results differed very greatly. The work of the Sub-Committee has, therefore, been directed to discovering the cause of the differences, and in the end they have defined a form of test which if strictly followed will always yield results in near agreement for a given sample of cod-liver oil in the hands of different workers.

In examining cod-liver oil by this test, a blue colour is produced which is compared with graded colour glasses such as the Lovibond colour glasses. The limit recommended in the test as described below corresponds to a colour similar to that of a Lovibond blue glass given the value 6·0.

The test, as recommended by the Sub-Committee, is a limit test, which does not require any precise determination of the blue value of cod-liver oil expressed in terms of a scale like the Lovibond scale. Since, however, this test is often used for making such precise determination, the Sub-Committee wish to point out how desirable it is for different workers to adhere closely to the conditions proposed. They also wish to point out how undesirable is the practice which has arisen of speaking of the colour value of cod-liver oil in terms of blue "units." The Sub-Committee feel that the term "blue unit" should give place to the term "blue value." The figure given to a glass on the Lovibond scale represents merely a grading in a series of glasses, and does not represent an amount of biological activity. The term "unit" used in measuring various therapeutic substances whose activity can only be determined biologically, means a definite amount of biological activity, and its application to the blue glass used for this cod-liver oil test has produced very great confusion of thought.

ANTIMONY TRICHLORIDE TEST FOR COD-LIVER OIL.

0·04 grm. of cod-liver oil examined by the following method gives a blue colour not less saturated, that is to say, not paler, than that of a blue glass standardised to have the following properties on the system of colour measurement adopted at the National Physical Laboratory:

Colour quality: 0·137R + 0·271G + 0·592B
Photometric transmission: 34·0 per cent.

In the foregoing specification R, G and B, respectively, denote the colours of monochromatic radiations of wave-length 0·700μ, 0·546μ and 0·436μ, and the measurements both of colour quality and photometric transmission are presumed to be made with the National Physical Laboratory standard "white" light.

DESCRIPTION OF TEST.—Weigh 2·00 grms. into a narrow-necked 10 millilitre measuring flask; fill to the mark with *chloroform* at a temperature of 20° and mix. Measure, at 20°, 0·2 millilitre of the solution so prepared by means not less accurate than a 1 millilitre pipette, the graduated portion of which is at least 15 centimetres long, into a colourless rectangular cell of 10 millimetres internal measurement in the direction of observation (see below). Place the glass cell in a colorimeter designed for matching the colour of the solution against colour glasses. Add rapidly 2·0 millilitres of antimony trichloride reagent, in such a way that the solutions mix. Simultaneously

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* The Cod-liver Oil Colour Test Sub-Committee was appointed by the Commission to recommend a form of test for cod-liver oil depending on what is known as the antimony trichloride reaction. In appointing the Sub-Committee the Commission wished it to be understood that the inclusion of such a test in the Pharmacopoeia was not to be taken as necessarily indicating that the test afforded a measure of vitamin *A* content. The test, if included, might prove of value for indicating a limit of deterioration or as indicating a characteristic property of cod-liver oil.

The Sub-Committee consisted of Dr. J. H. Burn (Chairman), with Messrs. Bacharach, Carr, Cocking, Evers, Jowett, Tainsh and Rosenheim, with Dr. C. H. Hampshire (Secretary).

observe the development of a blue colour, which rapidly reaches a maximum and then fades. By means of combinations of graded colour glasses match the colour at the point of maximum intensity. It may be necessary to employ yellow and red as well as blue glasses. In order to obtain an accurate match it may be necessary to diminish the transparency on the side of the cell; this must be done by adding on that side neutral tinted glasses, the value of which should be disregarded.

Several preliminary observations should be made to enable subsequent readings to be taken without undue delay in arranging the glasses, and to determine how long after mixing is the point of maximum intensity of colour. The maximum intensity may develop within ten secords, but the time varies with different oils. It is of the greatest importance that the observer should satisfy himself that the final match is made at the point of maximum intensity of the blue colour. Neither the reagent nor the solutions should come into contact with rubber.

ANTIMONY TRICHLORIDE REAGENT.—A solution of *antimony trichloride* in pure dry chloroform saturated at 20° is prepared in the following way: Wash *chloroform* two or three times with its own volume of distilled water, dry the chloroform over *anhydrous potassium carbonate*; pour off and distil, rejecting the first 10 per cent. of the distillate. During drying and distillation protect the chloroform from light. Wash *antimony trichloride* with the pure dry chloroform until the washings are clear. Prepare a solution, saturated at 20°, of the washed antimony trichloride in the pure dry chloroform. The solution, which must contain not less than 21 and not more than 23 per cent. w/v of $SbCl_3$, should be kept in a well-stoppered bottle of amber-coloured glass.

Assay.—Mix 1 millilitre with a solution of 2 grms. of *sodium potassium tartrate* in 20 millilitres of *water*; rotate the mixture, add 2 grms. of *sodium bicarbonate* and titrate with *N*/10 *iodine*. Each millilitre of *N*/10 *iodine* is equivalent to 0·01141 grms. of $SbCl_3$.

NOTE BY THE PHARMACOPOEIA COMMISSION.

COD-LIVER OIL—VITAMIN *D*.—The Pharmacopoeia Commission have considered the question of making a requirement for the amount of vitamin *D* in cod-liver oil. The evidence brought before the Commission hitherto has led to the provisional conclusion that it is not necessary to make such a requirement. The main grounds for this conclusion are—(1) That although there may be considerable variation in the amount of vitamin *D* present in different samples, almost all samples contain enough for therapeutic purposes; (2) That the estimation of vitamin *D* is an expensive and time-consuming process which should not be required unless absolutely necessary.

In view, however, of the increasing practice of stating the vitamin *D* potency on the label of bottles of cod-liver oil, and of the desirability of uniformity in the expression of this potency, the Commission are considering an addition to the requirements which will define the Standard Preparation and the Unit, and indicate the methods of assay which are to be used by those who wish to make a biological estimation of vitamin *D* in samples of cod-liver oil. If this addition is made, the Standard Preparation and the Unit will be those recently defined by the Medical Research Council.

Cyprus.

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1929.

THE Government Analyst, Dr. S. G. Willmott, reports that of the 1713 samples examined during the year, 1665 were official, including 406 exhibits in criminal cases and 469 foods and drugs. The number of food and drug samples showed a decrease of 384, compared with the previous year, and the adulteration had increased from 8·3 to 10·5 per cent.

The method of taking official samples of food and drugs in Cyprus leaves much to be desired. First, it is doubtful whether the small sum of £20 is adequate to cover all expenses incurred in the collection of a satisfactory number of samples of food and drugs (including milk and aerated waters) for the whole Island, in any one year.

Secondly, the present practice of the police in sending for analysis large numbers of samples from all six administrative districts at practically the same time, is most unsatisfactory from every point of view. In the past, samples appear to have been submitted only about three times per year.

The result is that, during the intervening period, the public is not protected against the adulteration of their food. This difficulty could be easily overcome, without increase in expenditure, by the simple expedient of taking fewer samples at more frequent intervals throughout the year. For a proper control over the food-supply, some samples should be sent for analysis every week. The present system also has the effect of temporarily dislocating the work of the Laboratory, because anything upwards of 250 samples of food and drugs may accumulate in the course of one week. The examination of such a number involves weeks of work, and could be avoided by the remedy indicated.

Thirdly, the genuineness of the food-supply is well protected by the system of taking surprise samples. The shopkeeper is not likely to practise adulteration if he is aware that an official sample may be taken at *any* time, and not merely at three expected times, as under the present system. This method also allows more latitude of action. For example, it was observed, in the course of a toxicological investigation, that a certain sample of coffee sent in by the police as an exhibit was adulterated with starch. This information was duly communicated to the Local Commandant, Military Police, with the suggestion that an official sample of the coffee in question should be taken under the Food and Drugs Law. The reply received was that no action could be taken in the matter, since the funds allocated for the year were exhausted.

It seems probable that the appointment of a food inspector would eradicate most of the shortcomings of the present system, and without additional expenditure. It should not be difficult to nominate a reliable member of the police force for this special duty, who could be trained to take official samples of the right foods at the right times. There is nothing original in the idea, which has been successfully put into practice in nearly every civilised country, and the Government is urged to give this suggestion the most careful consideration.

COFFEE.—Of the 112 samples analysed, 13 were adulterated with roasted wheat ground to a fine powder; this is the usual method of adulterating coffee in Cyprus.

OLIVE OIL.—Fifty-one samples were analysed, and the adulteration rose to the unusually high figure of 37·2 per cent., owing to the poor olive harvest of 1928–1929, and the consequent rise in price. The adulterants found were cotton-seed oil, arachis oil and "cocolina."

Fertilisers and Feeding Stuffs.

Merchandise Marks Act.

STATUTORY RULES AND ORDERS, 1931, No. 171.

THE MERCHANDISE MARKS (IMPORTED GOODS) No. 7 ORDER, 1931.*

At the Court at Buckingham Palace, the 20th day of March, 1931.

Present: The King's Most Excellent Majesty in Council.

Whereas by sub-section (1) of Section 2 of the Merchandise Marks Act, 1926 (16 & 17 Geo. 5, c. 53), it is provided that after an enquiry in relation to goods of any class or description has on a reference from the appropriate Department been held by a Committee appointed for the purposes of the said Act and the report of the Committee on the matter has been taken into consideration by the Department, that Department may, unless it appears to them that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if imported goods of that class or description for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, make a representation to His Majesty that it is desirable that an Order should be made under the said Section 2, and His Majesty in Council may thereupon, subject to the provisions of the said Act, make an Order prohibiting the sale or the exposure for sale in the United Kingdom of imported goods of that class or description unless they bear an indication of origin:

And whereas in accordance with the provisions of the said Section an enquiry in relation to the class or description of goods to which the present Order relates, has on reference from the appropriate Department, namely, the Board of Trade (hereinafter called the Board), been held by a Committee appointed for the purposes of the said Act and the report of that Committee has been taken into consideration by the Board:

And whereas by sub-section (5) of Section 2 of the said Act it is provided that if on an enquiry under sub-section (1) of the said Section it appears to a Committee to be desirable that any imported goods should bear an indication of origin at the time of importation, and the Committee so reports to the appropriate Department, that Department, unless, having regard to all the circumstances of the case including the re-export trade of the United Kingdom in that class or description of goods, it considers such action undesirable, may make a representation to His Majesty that it is desirable that the goods should bear an indication of origin at the time of importation, and His Majesty may by Order in Council under the said Section (without prejudice to His Powers under sub-section (1) of the said Section) make provision accordingly:

And whereas it does not appear to the Board that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if the goods described in this Order imported for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, and the Board have accordingly made representations to His Majesty that it is desirable that an Order should be made under the said Section 2.

And whereas the Committee have reported to the Board that it appears to them to be desirable that the goods described in this Order should bear an indication of origin at the time of importation:

And whereas the Board having had regard to all the circumstances of the case including the re-export trade in those goods have made representations to His Majesty that it is desirable that the goods described in this Order should bear an indication of origin at the time of importation:

Now, therefore, His Majesty, by and with the advice of His Privy Council, in pursuance of the powers vested in Him by the said Section and of all other powers enabling Him in that behalf is pleased to order, and it is hereby ordered, as follows:—

1. It shall not be lawful to import into the United Kingdom any of the fertilisers or feeding stuffs specified herein or to sell or expose for sale in the United Kingdom any such fertilisers or feeding stuffs which have been imported unless they bear an indication of origin.

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* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1d. net.

2. This Order applies to fertilisers and feeding stuffs of the following descriptions:—

(*a*) Bone meal and bone flour whether raw degreased or degelatinised;

(*b*) hoof meal, horn meal and mixtures thereof;

(*c*) meat meal, meat and bone meal and carcase meal;

(*d*) dried blood, whether ground or unground.

3. The indication of origin shall be printed, stamped, stencilled, painted or branded on the bag, sack, cask, keg or other container in which the goods are imported or sold or exposed for sale.

4. Nothing in this Order shall require any such fertilisers or feeding stuffs to bear an indication of origin on sale when the total quantity sold does not exceed 14 lbs. in weight.

5. Goods to which this Order applies shall bear the indication of origin herein provided on exposure for sale wholesale whether or not the person so exposing the goods is a wholesale dealer.

6. This Order shall come into force at the expiration of three months from the date hereof.

7.—(*a*) This Order may be cited as the Merchandise Marks (Imported Goods) No. 7 Order, 1931.

(*b*) The Interpretation Act 1889(*a*) shall apply to the interpretation of this Order as it applies to the interpretation of an Act of Parliament.

M. P. A. HANKEY.

(a) 52–3 Vict. c. 63.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Refractometric Studies on Fruit Juices. H. Eckart. (*Z. Unters. Lebensm.*, 1931, **61**, 346–353.)—The following values of n_D at 16° to 20° C. are given for the freshly-prepared juices during the season July–October, 1930 (*cf.* ANALYST, 1926, **51**, 40):—Wild raspberry (sp. gr. 1·0440) 1·3480, (sp. gr. 1·039) 1·3462, (sp. gr. 1·025) 1·3422; garden raspberry (sp. gr. 1·0400) 1·3448; wild strawberry (sp. gr. 1·0390) 1·3460; garden strawberry (sp. gr. 1·052) 1·3439; red currant (sp. gr. 1·0410) 1·3471; white currant (sp. gr. 1·0444) 1·3475; black currant 1·3548; gooseberry 1·3503; bilberry 1·3408; blackberry 1·3412; cranberry 1·3460 and 1·3595; Sicilian lemon (sp. gr. 1·0340) 1·3438; Sicilian orange (sp. gr. 1·0520) 1·3519; acid cherry (sp. gr. 1·0640) 1·3561; sweet cherry (sp. gr. 1·0850) 1·3629; Italian grape 1·3645; Cornelius cherry 1·3702; elderberry 1·3551. The values vary over only a small range for juices made on successive days over a period of 1 month, and may be taken as characteristic for the season. Rejected juices had values 0·005 low, and addition of 250 c.c. of water to 250 c.c. of wild raspberry juice lowered n_D from 1·3473 to 1·339 (to 1·3452 for addition of 25 c.c. to 250 c.c. of juice). Readings taken every 2 days for a month on the same stored juice showed a fall in n_D of 0·017 to 0·003 at the end of the period, and indicate the influence of autofermentation on storage. The Zeiss hand-refractometer designed for sugar control is recommended, and may be adapted to give direct readings of the dry solids.

J. G.

Quartz Crystals in Honey. F. E. Nottbohm and F. Lucius. (*Z. Unters. Lebensm.*, 1931, **61**, 320–321.)—Particles of sand in honey may be due to mechanical inclusion or may be carried in the pollen or nectar. The possibility of the deposition of undigestible siliceous material by the bees suggested by Elser (*id.*, 1930, **60**, 332) is discussed, and Elser's observations are criticised in that the hydrochloric acid-insoluble portion of the residue from the honey, after extraction with water, is regarded as silica, instead of the acid-insoluble portion of the ash. The authors find only 0·01 per cent. of acid-insoluble ash (corresponding with about 0·005 mgrm. of silica from one bee), and cannot regard the visible sediment, obtained by Elser on allowing the honey to stand, as quartz crystals. J. G.

Iodimetric Determination of Reducing Sugars in the Apple. H. K. Archbold and E. M. Widdowson. (*Biochem J.*, 1931, **25**, 101–116.)—The oxidation of glucose and fructose by alkaline iodine at 1° C. and methods of preparation of apple extracts for iodimetric determinations have been investigated. Glucose is quantitatively oxidised to gluconic acid in two hours at 1° C., and some oxidation of fructose also occurs. The theoretical amount (1·410 grm.) of iodine is reduced per 1 grm. of glucose. In mixtures of glucose and fructose the amount of iodine reduced per grm. of fructose increases from 0·013 grm. to 0·017 grm. as the ratio of fructose to glucose increases from 1:1 to 5:1, and then decreases slowly as this ratio is further increased. The value 0·017 can be used for determination of fructose and glucose in apples by combination of the iodimetric and copper reduction methods, since the ratio of fructose to glucose in the apple is about 4:1. The amounts of fructose and glucose are then calculated by solving the simultaneous equations used by Evans (*Ann. Bot.*, 1928, **42**, 1): (1) $C_1x - C_2y$=iodine value per 100 c.c. of solution, and (2) $K_1x - K_2y$=copper reducing power of 100 c.c. of solution, where C_1 and C_2 are the grms. of iodine reduced per grm. of glucose and fructose, respectively, and K_1 and K_2 the grms. of cuprous oxide formed per grm. of glucose and fructose at the dilution used. The new and more accurate values 1·410 and 0·017 are used for C_1 and C_2. The presence of oxidisable material, other than sugar, makes it necessary to clear the apple extracts before carrying out iodimetric determinations. Basic lead acetate, with either sodium phosphate (Na_2HPO_4) or potassium oxalate as the de-leading agent, was found to give satisfactory results with extracts prepared from mature apples. The loss of sugar during clearing, and the slight action of iodine on potassium oxalate, make corrections necessary for both the copper-reducing value and the iodine value, if oxalate is used to remove the lead. If sodium phosphate is used there is no loss of sugar, but the cleared solution is yellow and still contains some non-sugar substance oxidisable by iodine. The solution can be decolorised by boiling with charcoal and satisfactory results obtained. Copper reduction determinations can be carried out on the yellow solution. With very immature apples coloured solutions are also obtained when potassium oxalate is used, and these solutions cannot be boiled, as an increase in the iodine value occurs owing to some action of oxalate on the sugars. Sodium phosphate has, therefore, been adopted as the de-leading agent for routine work.

P. H. P.

Selective Fermentation. Alcoholic Fermentation of Mixtures of Glucose and Fructose by Brewer's and Sauterne Yeasts. R. H. Hopkins. (*Biochem. J.*, 1931, **25**, 245–255.)—Experiments by the author on selective fermentation of mixtures of glucose and fructose by brewer's and Sauterne yeasts gave the following results:—The factor $K_{G/F}$ for brewer's yeast was not appreciably influenced by the relative proportions of glucose and fructose in the original solution. The factor was not influenced by modification of the saccharase activity of brewer's yeast by the method of Willstätter, Lowry and Schneider (*Z. Physiol. Chem.*, 1925, **146**, 158; **150**, 287). The saccharase of Sauterne yeast resembled that of brewer's yeast in that it was inhibited more strongly by fructose than by glucose. The addition of saccharase to a mixture of glucose and fructose undergoing fermentation by zymin (brewer's) did not affect the selective fermentation of the two sugars. The factor $K_{G/F}$ for brewer's yeast decreased with rise in temperature of fermentation, whilst that for Sauterne yeast increased. Brewer's yeast ferments glucose faster than fructose in separate solutions when the concentration of sugar is less than 1 per cent. Sauterne yeast ferments fructose faster than glucose in separate solutions at all concentrations up to 10 per cent., but especially at low concentrations. The muta-rotation of partly fermented solutions of the sugars is for both sugars by brewer's yeast in the positive, and by Sauterne yeast in the negative direction. The hypothesis is now advanced that brewer's yeast, and presumably most yeasts, are specific for that form of fructose which is present in small proportion, but which increases with temperature, possibly a γ-form, whereas Sauterne yeasts are specific for the normal form. If this hypothesis should prove correct, the problem of the selective fermentation of these sugars by various yeasts resolves itself into finding an explanation for the fact that brewer's and most yeasts are specific for certain hexoses, namely, those derived directly from maltose, sucrose, etc., and Sauterne yeasts for normal fructose as it occurs in grapes. P. H. P.

Composition of Commercial Palm Oils. II. The Fatty Acids and Component Glycerides of some Palm Oils of High Free Acidity. T. P. Hilditch and E. E. Jones. (*J. Soc. Chem. Ind.*, 1931, **50**, 171–176T.)—The previous communication dealt with samples of palm oils of relatively low acidity (ANALYST, 1930, **55**, 701), and similar analyses of the mixed fatty acids of other four palm oils of much higher acidity have now been made. With increasing free acidity the determination of the saturated acids (mainly myristic) becomes more difficult, owing to the presence of small amounts of decomposition products, the boiling point of which is about 35° to 100° C. at 1 mm., and although the greater part of the myristic acid is usually retained in the "solid" acids (which were not appreciably contaminated with rancidity products), yet the determination is not so close as that of palmitic, stearic or oleic acid. The neutral fats were prepared by adding saturated sodium carbonate solution to the ethereal solution of the fat, and, after settling without shaking, running off and repeating the addition until the mixture was alkaline to phenolphthalein, after which the next addition of sodium carbonate solution was gently shaken with the fat and the final addition

vigorously shaken. Residual soap was washed out and small amounts of neutral fats carried down by the soap were recovered by extraction with ether. The estimated composition of the four oils, omitting unsaponifiable matter, was:

	Myristic. Per Cent.	Palmitic. Per Cent.	Stearic. Per Cent.	Oleic. Per Cent.	Linoleic. Per Cent.
Bonny Old Calabar.					
Crude	4·1	40·1	4·4	41·5	9·9
Neutralised ..	2·5	40·8	4·3	42·5	9·9
Benin.					
Crude	4·5	37·5	4·2	47·3	6·5
Neutralised ..	4·9	39·1	2·3	45·5	8·2
Niger.					
Crude	5·9	39·3	2·2	42·7	9·9
Neutralised ..	3·2	36·0	4·1	46·9	9·8
Drewin "Gold Coast."					
Crude	2·2	35·3	5·2	52·3	5·0
Neutralised ..	3·0	33·6	5·3	52·3	5·8

It would seem that hydrolysis caused by rancidity proceeds, on the whole, non-selectively, the only exception being the Niger oil, and this may be due to some accidental cause. Considering the eight palm oils together, they are divisible into two classes; the Drewin (Gold Coast) oils containing 35 per cent. or less of palmitic and 50 to 52 per cent. oleic acid, and the remainder about 40 per cent. palmitic and 40 to 45 oleic. Similarly, the total percentage of saturated acids for the Gold Coast oils is about 42, and that of the other types 46 to 48·5, and the association ratio is 0·8 for the former and 1 for the others. Possibly the Drewin oils may be from different botanical species of oil palm. The extreme limits for stearic acid are 2·2 to 7·5 per cent. Such variation as there is in the component fatty acids of palm oil involves alteration both in the amount of palmitic acid and of the total acids of the C_{18} series, which is a point of difference from animal fats. The observed acetyl values of the neutralised oils varied from 11·0 to 26·3, except for the Niger oil, which had the value 51·4. These values for the high acid oils are low compared with those calculated from the free acid content, so that, for the most part, the fats have been completely hydrolysed to glycerol and fatty acids, the proportion of semi-hydrolysed mono- or di-glycerides indicated by the acetyl values being comparatively small for Bonny Old Calabar, Benin and Drewin No. 2. The plantation oils of lowest free acidity had acetyl values of 11 to 12, indicating the presence of some mono- or di-glycerides in the fresh fat as matured in the palm fruit, the amount corresponding with 4 to 8 per cent. of the oil expressed as diglyceride. D. G. H.

Quantitative Determination of Lecithin in some Fats. E. Foyn. (*J. Pharm. Chim.*, 1931, **123**, 465–474.)—The lecithin was determined by weighing about 5 grms. of the fat in a narrow glass tube, and pouring it, drop by drop, into

30 c.c. of fuming nitric acid in a 500 c.c. flask, finally dropping in the tube. Oxidation is brought about by warming for 30 minutes, after which the solution is evaporated on a water-bath, 6 c.c. of 10 per cent. nitric acid added to the residue, the whole mixed, placed on ice, and the solidified organic acids then washed on a filter paper with water acidulated with nitric acid. The liquid is filtered, concentrated to 10 c.c., transferred to a flask, and precipitation brought about by 30 c.c. of molybdic solution, and, after warming for 15 minutes, the liquid is left overnight, after which it is filtered, and the precipitate collected in a tared Gooch crucible and washed with a 5 per cent. solution of ammonium nitrate in 1 per cent. nitric acid until the excess of the molybdic solution is removed, when 60 per cent. alcohol is used to remove the ammonium nitrate, followed by 96 per cent. alcohol, and, finally, one washing with ether, after which the precipitate is dried and weighed. Taking the formula for lecithin as $C_{44}H_{86}NPO_9$, and that of the molybdic precipitate as $(NH_4)_3PO_4,12MoO_3$, the lecithin is found by multiplying the weight of the precipitate by the factor 0·4287. For identification of the fatty material analysed the iodine value was determined by Margosches' method (*Die Jodzahlschnellmethode und die Ueberjodzahl der Fette*, Stuttgart, 1927), in which 0·1 to 0·12 grm. of liquid oil, or 0·2 to 0·4 of fat, is completely dissolved in 10 c.c. of absolute alcohol, and 25 c.c. of 0·2 *N* alcoholic iodine added, followed by 200 c.c. of warm water. After shaking and leaving for 10 minutes the excess of iodine is titrated. Figures so obtained were very similar to those given by the Hübl method. The proportions of lecithin and of nitrogen, and the iodine values of a large number of vegetable and animal fats are given, varying from 0·6 per cent. of lecithin in linseed oil to 0·04 in refined coconut oil, and 0·063 in cod-liver oil, to 0·017 in whale oil free from sediment. Lecithin is constantly present in small quantities in vegetable and animal fats, and appears to be dissociated from a more complex compound during the extraction of the fat; hence, two samples of a fat may not invariably give similar figures. The figures obtained by the above methods are comparable among themselves and approach the real values. The figures obtained for nitrogen were always higher than would be accounted for by the nitrogen in lecithin. D. G. H.

Fat and Phosphatid Contents of Cacao Beans. B. Rewald and H. Christlieb. (*Chem. Ztg.*, 1931, **55**, 393–394.)—In 17 samples of raw, dehusked cacao beans grown in various parts of the world, the moisture content varied from 3·8 to 6·6 per cent., the average being 5·2 per cent. The fat content of the water-free beans ranged from 52·7 to 61·9 per cent., the average value being 56·3 per cent. It is assumed that a lower percentage of fat than 50 per cent. should not occur normally. The phosphatid content showed limits of 0·02 and 0·256 per cent. (dry beans), the average being about 0·1 per cent. Owing to the fact that it simplifies production considerably, 0·1 to 0·5 per cent. of plant lecithin is often added during the manufacture of chocolate.

To determine the phosphatids, the powdered beans were extracted with a mixture of benzene (8 parts) and alcohol (2 parts), from 6 to 8 extractions being

found necessary. After evaporation of the solvent, the mixture of fat and phosphatids was taken up in ether and, after distillation of the ether, filtered until bright. From 6 to 8 grms. of the filtrate were treated in a Kjeldahl flask with 40 c.c. of Neumann's acid mixture, fuming nitric acid being added and heat applied, at first gently and later with a larger flame, until the liquid became perfectly clear and colourless. The cold liquid was diluted with 100 c.c. of water, and the phosphoric acid precipitated by means of ammonium molybdate. The next day the precipitate was collected on a Gooch crucible, washed with water until this showed a neutral reaction, returned to the Kjeldahl flask, and dissolved in excess of 0·25 *N* sodium hydroxide. The ammonia liberated was boiled off, and the cooled residual liquid titrated with 0·25 *N* sulphuric acid to determine the excess of alkali remaining. The basis of the calculation is the presence of 3·94 per cent. of phosphorus in lecithin (calculated from the formula for egg-yolk). Contrary to the statement of Fincke (*Die Kakaobutter und ihre Verfälschungen*, 1929), the whole of the phosphatids are completely extractable from cacao beans by the procedure described above. T. H. P.

Detection of Benzoic Acid as Methyl Ester. L. Pick. (*Z. Unters. Lebensm.*, 1931, **61**, 358.)—A modified form of Röhrig's method (*id.*, 1908, **15**, 27; *cf.* Fischer and Gruenert, ANALYST, 1909, **34**, 394) avoids the difficulty due to the odour of substances natural to (*e.g.*) wine and meat products. Wine is extracted with ether or petroleum spirit in the presence of sulphuric acid, the extract made alkaline with sodium hydroxide and evaporated, and the residue gently warmed over the naked flame to remove any substances contributing aroma. A drop of dimethyl sulphate is added, and, on stirring for 1 minute, the characteristic smell of the methyl ester is produced from 10 mgrms. or more of benzoic acid. If necessary, the ester may be separated by extraction in ether in the manner described by Röhrig, when 1 mgrm. of benzoic acid is detectable. Meat products (*e.g.* 80 grms.) are minced, an equal weight of 2 per cent. sodium carbonate solution added, and the mixture strained through a cloth, the residue washed with water, and the extract filtered. Fatty acids are then removed by precipitation with calcium chloride or with lime, and the filtered liquid evaporated, acidified, and extracted with ether as with wines (sensitiveness 0·07 per cent.). Salicylic and *p*-hydroxybenzoic acids do not interfere, but in the presence of large amounts of chlorides the odour of methyl chloride is obtained. J. G.

Colour Reaction of some Drugs. J. Sivadjian. (*J. Pharm. Chim.*, 1931, **123**, 528–529.)—Uroselectan (sodium 5-iodo-2-hydroxy-pyridine acetate) gives a yellow precipitate with a 5 per cent. solution of ferric chloride, and a green-yellow coloration when treated with hydrogen peroxide containing 4 per cent. of sodium chloride. If 6 to 7 drops of bromine water are added to a few mgrms. of uroselectan dissolved in water, a Prussian blue coloration results, which, on addition of concentrated sulphuric acid, disappears and a precipitate forms. Ammonia brings back the blue colour, but if the ammonia is present in excess the

colour changes to pink. If plasmoquin and percaine are treated with tetrachlorobenzoquinone of chloranil in the presence of acetic acid, and the mixture boiled, a blue colour results with plasmoquin, and there is no change in colour with percaine. If, however, the reaction occurs in the presence of epichlorhydrin, acetic acid is not necessary, and percaine gives an emerald-green colour. If an ammoniacal solution of pyrocatechin is boiled with a little nitroprusside a cherry-red colour results. D. G. H.

Sivadjian's Colour Reaction for Identifying Ephedrin. W. H. Hartung, F. Crossley and J. C. Munch. (*J. Pharm. Chim.*, 1931, **123**, 474–478.)—Sivadjian's reaction for identifying ephedrin (ANALYST, 1930, **55**, 763) was found to give less intense colours if the U.S.P. hydrogen peroxide was used in place of that from the Rhône-Poulenc works, but, if carried out as follows, intense and reproducible colours are obtained:—The substance is examined in a 0·1 *M* solution, and all amines are converted into their acid hydrochlorides. The solution (0·5 c.c.) is treated in a 10 × 100 mm. test tube with 4 c.c. of a 16 per cent. solution of sodium chloride, 0·45 c.c. of a 0·1 *N* alkali solution, and 6 drops of a 39 volume solution of hydrogen peroxide. After shaking, the tube is kept in boiling water for 2 minutes, when the colour reaches its maximum and remains so for about an hour at laboratory temperature. The colours given by 31 different substances are described according to the plates published by Mulliken in "Identification of Pure Organic Compounds," Vol. III. Sivadjian's colour reaction is not specific for the amino-alcohols of the ephedrine type; phenyl-ethanolamine gives a colour reaction, as also do amino-acetones, but the colorations with these are less intense than those with their corresponding alcohols. Aliphatic amino-alcohols or alcohols give no colorations, the presence of the aromatic nucleus appearing to be essential. The amino group intensifies the reaction, and the effect is greater if it is linked to the ring than to a side chain. Phenol gives a more intense reaction than aniline. The presence of a carboxyl group in a side chain inhibits the reaction. The reaction may thus be used to differentiate the isomeric toluidines, and the three amino-phenols. D. G. H.

Determination of Santonin in "Trochisci Santonini." P. J. Claus. (*Pharm. Weekblad*, 1931, **68**, 414–424.)—The Dutch official method and its modifications are described and criticised, and the following procedure suggested for mixtures of santonin and cocoa-butter (*e.g.* worm-tablets): The weighed sample (containing about 100 mgrms. of santonin) is dried at 105° C., ground, extracted for 5 hours in a Soxhlet apparatus with ether, and the extract filtered and evaporated, 0·5 grm. of paraffin-wax being added to the residue, to promote subsequent flocculation of the cocoa-butter. The residue is boiled with 50 grms. of alcohol (80° Gay–Lussac=sp. gr. 0·86416 at 15° C.) for 30 minutes under a reflux condenser, the cooled extract filtered on a paper wetted with the alcohol, and the residue re-extracted with 15 grms. of alcohol, both filtrates being collected in a separating funnel. They are then shaken with 15 grms. of petroleum spirit

(b.pt., 40° to 70° C.), the alcohol removed, the petroleum layer washed with 15 grms. of alcohol, and the total alcoholic liquid warmed for a short time to remove any petroleum spirit which otherwise interferes with the final titration. The mixture is then neutralised at room temperature to phenolphthalein with 0·1 *N* sodium hydroxide solution, 10 c.c. added in excess, and sodium santoninate produced by boiling under a reflux condenser for 20 minutes. The amount of alkali consumed is determined by titration in the cold with 0·1 *N* hydrochloric acid, and 1 c.c. 0·1 *N* sodium hydroxide solution ≡ 24·6 mgrms. of santonin. Allowance should be made for the alkali used up in a blank experiment (0·3 c.c. for a pyrex flask). When 50 to 150 mgrms. of santonin were taken, the results were 2 per cent. low. If ether is replaced by chloroform, the results are high (about 5 mgrms.), since this solvent reacts with the alkali

$$(CHCl_3 + 4NaOH = HCO_2Na + 3NaCl + 2H_2O).$$ J. G.

Podophyllum Rhizome—American and Indian. T. E. Wallis and S. Goldberg. (*Quart. J. Pharm.*, 1931, **4**, 28–32.)—For determining the crude fibre in vegetable drugs, the following modification of the Dutch method, which is more efficient than the official method of the Ministry of Agriculture, is suggested: About 2 grms. of the material in No. 60 powder are treated with 50 c.c. of 10 per cent. nitric acid solution in a 200 c.c. flask, which is immersed during 15 minutes in a boiling water bath. The liquid is stirred meanwhile with a glass stirrer making 160 revolutions per minute. The contents of the flask are next transferred rapidly to a fine cloth strainer and filtered by suction. The residue is washed with 100 c.c. of boiling water, restored to the digestion flask, and heated and stirred as before with 50 c.c. of 2·5 per cent. sodium hydroxide solution. After a second filtration and washing, the residue is digested with 50 c.c. of 1 per cent. sulphuric acid solution, and again filtered and washed. The fibre is then placed in a weighed Berlin porous silica-bottomed crucible, dried to constant weight at 100° C., ashed, and the crucible again weighed. The difference between the last two weights gives the weight of crude fibre.

The crude fibre obtainable from American podophyllum (from *Podophyllum peltatum*, Linn.) by this procedure amounted to 5·35 per cent., whereas the Ministry of Agriculture process gave 7·5 per cent. The Indian drug (from *P. Emodi*, Wallich), the resin of which is about twice as active as that of the American variety, gave 7·2 and 10·5 per cent., respectively, by the two methods. When the drug was subjected to a preliminary exhaustion with 90 per cent. alcohol, the crude fibre obtained by the modified Dutch process from moisture-free American (Indian) podophyllum was 5·3 (6·7) per cent.

A commercial sample of powdered American podophyllum yielded 8·7 per cent. of crude fibre by the modified Dutch method, and was found to contain both Indian podophyllum and guaiacum wood (about 10 per cent.). A satisfactory reagent for identifying, and distinguishing between, the resins of the two drugs is 5 per cent. aqueous copper acetate solution, which gives a bright green coloration with an alcoholic (90 per cent.) solution of the resin of *P. peltatum*, and a brown

precipitate with a similar solution of the resin of *P. Emodi*. A detailed account of the anatomy of the two varieties of podophyllum, and of the structures by means of which they may be differentiated in the form of powder, is to be published shortly.

T. H. P.

Studies on the Gums. II. Tragacanthin—The Soluble Constituent of Gum Tragacanth. A. G. Norman. (*Biochem. J.*, 1931, **25**, 200–204.)—A brief outline is given of the literature on the subject of gum tragacanth, which, like that of the gums in general, is fragmentary and confused. A name has never been given to the constituent of gum tragacanth soluble in water, and it is proposed to term it tragacanthin. On addition of water gum tragacanth swells enormously, since the water-insoluble form, bassorin, constituting 60–70 per cent. of the gum, gives a very bulky jelly. The tragacanthin may be separated by ordinary filtration in extreme dilution. The dilute filtrate obtained is concentrated under reduced pressure and treated with acid alcohol. The precipitate formed is filtered off, dissolved in water, and precipitated again. After several such reprecipitations the final dried product is a fine white powder very readily soluble in water. Tragacanthin is also separated effectively when a solution of the gum is first made alkaline, and then just slightly acid, and centrifuged. Uronic acid residues are found to be present and to constitute about one-half of the molecule. Arabinose was the only sugar found; no galactose could be detected. It seems likely that tragacanthin consists solely of uronic acid and arabinose, although it is only possible to account for 94 per cent. of the molecule in this way. This is not in agreement with the conclusion of O'Sullivan (*J. Chem. Soc.*, 1901, **79**, 1164), who considered tragacanthin to be a complex poly-arabinon-trigalactan-geddic acid, yielding, on hydrolysis, arabinose, galactose and geddic acid, an isomer of arabic acid also obtained by him from certain constituents of gedda gum. Hydrolysis products were prepared, the analytical figures for which give rise to the suggestion that a portion of the arabinose is united to the uronic acid to form a resistant nucleus, and the residue attached by glucosidic linkage, and, therefore, easily removable.

P. H. P.

Electrometric Studies of Complex-Formation. II. Tartrates of Bismuth. C. Morton. (*Quart. J. Pharm.*, 1931, **4**, 1–13.)—The results of electrometric titrations confirm the existence of the four sparingly soluble bismuth tartrates described by Corfield and Adams (*Year Book of Pharm.*, 1923, 576; 1924, 594), the ratio $Bi:C_4H_4O_6$ having the values 1:1, 1:1·5, 1:2 and 1:2·5, respectively. These compounds, however, are not insoluble complex acids, but true salts of the weak acid with very weak base type. Their properties are satisfactorily accounted for on the assumptions that the 1:2·5- and 1:2-tartrates are acid salts of the formulae $Bi_2(C_4H_4O_6)_3$, $2C_4H_6O_6$ and $Bi_2(C_4H_4O_6)_3$, $C_4H_6O_6$, respectively; that the 1:1·5-compound is the normal tartrate, $Bi_2(C_4H_4O_6)_3$; and that the 1:1-tartrate is a basic salt, $Bi(OH)C_4H_4O_6$. The "bismuth and sodium tartrates," obtained by dissolving the insoluble tartrates in sodium hydroxide solutions, are equilibrated mixtures of the soluble basic complex, $2Bi(OH)_3$, $Bi(OH)C_4H_4O_6$, with sodium

tartrate, there being no evidence of the existence of complex anions in the neutralised solutions. In the absence of complex formation, the precipitation of basic salts of bismuth by the addition of alkali commences at pH 1·7; precipitation is delayed by the presence of glycerol, but eventually a highly basic precipitate is obtained. It is suggested that the method of Corfield and Adams for preparing the normal or 1 : 1·5-compound, namely, the interaction of solid bismuth oxynitrate, tartaric acid, and water, be adopted as the standard procedure, and that "bismuth and sodium tartrate" be obtained by neutralisation of this product, with subsequent evaporation. Methods involving the use of alcohol or other precipitants are shown to be unsound. T. H. P.

Biochemical.

Biochemistry of Aluminium. II. Excretion and Absorption of Aluminium in the Rat. K. Mackenzie. (*Biochem. J.*, 1931, **25**, 287–291.)—It has previously been shown by the author (*Biochem. J.*, 1930, **24**, 1433), by balance experiments with pigs, that practically the whole of the aluminium provided as a supplement to the diet is voided in the faeces. With such animals there is a difficulty in devising a ration free from aluminium, and accordingly this work has been supplemented by experiments with rats, in which the ration could be built up by the use of highly purified foodstuffs. The three materials likely to contain aluminium, namely, the food, the urine and the faeces, were kept as separate as possible by means of specially devised individual glass jars (in which the rats were kept) and special food troughs. The experiments showed that rats receiving a diet containing aluminium excrete the aluminium entirely by way of the alimentary tract, and there is no clear evidence that any of the aluminium is excreted in the urine. No definite evidence of absorption of aluminium by the internal organs of such rats has been established. Therefore, aluminium plays no important part in the metabolism of the rat. P. H. P.

Vitamin *A* Content of Oats. C. R. Meyer and R. A. Hetler. (*J. Agric. Res.*, 1931, **42**, 501–506.)—Whole hull-less oats and acetone-extracted oat oil were given to rats depleted of vitamin *A* as the sole source of that vitamin in their diet. Whole oats up to a level of 60 per cent. of the diet in no case cured ophthalmia, and death occurred before the eight-week test period was finished. A slight improvement in the eye conditions was noticed when oil at the high level of 30 and 50 per cent. of the diet was used, but growth was very slow or completely arrested, although the animals lived over the test period. It is concluded that a very small amount of vitamin *A* is present in oat oil. The rapid cure of ophthalmia and resumption of growth which occurred on adding cod-liver oil to the diet show that the bad effects were not due to any toxic effect of the oats or oat oil. D. G. H.

Spectrographic Data Concerning Vitamin *A* and Liver Oils. R. A. Morton, I. M. Heilbron and A. Thompson. (*Biochem. J.*, 1931, **25**, 20–29.)—This work was done in order to place on record a number of spectroscopic observations on liver oils and concentrates. The data are primarily concerned with

the more precise description of tests for vitamin *A*, in particular with the ultra-violet absorption and the blue colour test. In the second place spectrographic methods have been utilised for a more penetrating investigation of the wider problem of the constituents of liver oils and concentrates. In this way it was hoped to gain some insight into the sequence of changes culminating in the synthesis of fat-soluble vitamins or pro-vitamins in nature. Although it is too early to estimate to what extent this hope has been realised, a completely fresh aspect of the chemistry of vitamin-bearing oils emerges from the discovery of new and highly characteristic absorption spectra, which cannot be identified with the properties of the major constituents of liver oils. Precise spectroscopic data regarding the vitamin *A* ultra-violet absorption band are recorded. The vitamin *A* band at 328$\mu\mu$ is in a high degree continuous, and is found to be free from fine structure. Nearly all cod-liver oils exhibit selective absorption in the region 260–295$\mu\mu$. Spectroscopic examination of the blue solutions obtained with antimony trichloride discloses, with cod-liver oils giving a clear ultra-violet band at 328$\mu\mu$, a single sharp band at 604–608$\mu\mu$. This class comprises the majority of pale medicinal cod-liver oils, and the parallelism between blue colour and ultra-violet absorption is well marked without the introduction of correction factors. With crude cod-liver oils of high potency additional selective absorption between 565–585$\mu\mu$ is frequently observed in the blue solution. The blue solutions given with concentrates have the main band at 620–624$\mu\mu$ (the intensity varying directly with the intensity of the ultra-violet band at 328$\mu\mu$ in the original material), and many of them show a less intense band at 582–593$\mu\mu$. Vitamin *A* is decomposed on treatment with sodium ethoxide. Concentrates so treated yield acids characterised by a series of well-defined absorption bands with maxima near 394, 375, 350, 330, 316, 302, 282, 271 and 260$\mu\mu$. Similarly absorbing acids are produced by the ordinary saponification process, but evidence is adduced showing that these acids cannot be ordinary fatty acids, and that they are not present as simple glycerides in the oil itself. P. H. P.

Spectrographic Data of Natural Fats and their Fatty Acids in Relation to Vitamin *A*. A. E. Gillam, I. M. Heilbron, T. P. Hilditch, and R. A. Morton. (*Biochem. J.*, 1931, **25**, 30–38.)—A detailed investigation of the absorption spectra of natural fats and their related acids has been started, following the observation that vitamin *A* concentrates yield, on treatment with sodium ethoxide, acids of which the absorption spectra exhibit characteristic fine structure. Certain broad aspects of the problem are considered, and not only vitamin *A*-containing oils, but also typical vegetable fats have been examined. The absorption spectra of the total acids from cod-liver oil are characterised by sharp bands with heads at about 392, 375, 350, 330, 316, 302, 281, 270, 259 and 235$\mu\mu$, and correspond closely with those of the selectively absorbing acids from the vitamin *A* concentrates described by Morton, Heilbron and Thompson (*Biochem. J.*, 1931, **25**, 24). The absorption spectrum of a halibut-liver oil rich in vitamin *A* shows the characteristic vitamin band at 328$\mu\mu$, and a second small band at about

225$\mu\mu$. The acids obtained from this oil on saponification reveal bands with heads at identically the same positions as those of the cod-liver oil acids. The absorption curve for butter acids (butter being chosen to represent a non-liver animal fat containing vitamin *A*) shows five definite maxima, indicating the presence of small quantities of substances having the same bands as those shown by the cod- and halibut-liver oil acids. The spectrum of butter-fat in chloroform solution shows distinct selective absorption at 322, 309, 284, 274 and 231$\mu\mu$; these bands correspond with those of the acids in alcohol. The absorption spectra of the mixed acids from whale oil (a typical marine animal non-liver oil deficient in vitamin *A*) are shown to be qualitatively, and roughly quantitatively, comparable with the cod- or halibut-liver acids. The oil itself, like butter, also has selective absorption similar to that of the acids, but different in intensity. It is shown that, as with butter, the selective absorption of the whale oil is not exclusively due to hydrolytic products of the fat. The absorption spectra of the mixed fatty acids of a Thresher shark-liver oil, from which vitamin *A* is absent, show ill-defined maxima at 270, 280 and 315$\mu\mu$, and a prominent band at 230$\mu\mu$. The absorption spectra curves of olive oil and its mixed acids and cottonseed oil and its acids are shown. The curves differ markedly from those shown by the vitamin *A*-containing liver oils and the corresponding acids of the latter. The vegetable oils exhibit a triplet group of bands with heads at 260, 271 and 281$\mu\mu$, and indications of other absorption in the region 300–350$\mu\mu$, but the typical vitamin *A* band is absent. The curves for the corresponding mixed acids, somewhat surprisingly, show less fine structure between 260–280$\mu\mu$ than those for the respective oils. From results obtained it is improbable that the recorded fine structure can be attributed to esters of highly unsaturated acids ("clupanodonic" type). The simplest explanation in consonance with all the facts so far observed is that under hydrolytic conditions a substance (or substances) accompanying vitamin *A* gives rise to acid decomposition products which display intense selective absorption. Sufficient of this acidic decomposition product is formed under the ordinary mild conditions of saponification to give rise to the observed spectra. That the acid decomposition products are in some way connected with the presence of vitamin *A* is indicated by the distinctly different absorption curves obtained with the acids from the non-vitamin *A*-containing olive or cottonseed oils. The fatty acids (or esters prepared therefrom) produced in the ordinary hydrolysis of vitamin *A*-containing liver oils, or of some other fatty oils from animals whose liver oils contain vitamin *A*, yield highly characteristic banded absorption spectra which are absent from the corresponding acids of vitamin *A*-free oils. P. H. P.

Colour Reactions of Sterols with Nitric Acid. O. Rosenheim and R. K. Callow. (*Biochem. J.*, 1931, **25**, 74–78.)—From a chance observation it was found that nitric acid gives characteristic colour reactions with certain sterols; a systematic study of the reaction was, therefore, made. The colours produced were found to be transient when pure colourless nitric acid was used, but more stable when a mixture of glacial acetic acid and nitric acid (1:4) was

employed. Finally, it was found that nitric acid which contained the acetates of certain metals gave fairly stable colour reactions. A solution of mercuric acetate in nitric acid ("mercury reagent") is recommended as a general reagent. For its preparation 25 grms. of mercuric acetate are dissolved in 100 c.c. of nitric acid (sp. gr. 1·42). Nitrous acid interferes with the colour reactions, and it is necessary to decolorise the solution with a few crystals of urea. When this precaution is used the reagent apparently keeps indefinitely. The reaction is carried out by the addition of an equal volume of the reagent to a chloroform solution of the sterol, and immediate shaking. On account of the high specific gravity of the mercury reagent, the mixture separates rapidly into an upper coloured chloroform layer and a lower, usually colourless, layer of the reagent. A red colour with the mercury reagent indicates the presence of the $\Delta^{1,2}$ (or $\Delta^{1,13}$) linkage in sterols; red colours are given by *allo*-cholesterol, *allo*-sitosterol, cholesterilene, ψ-cholestene and β-cholesterol. The tint of the red colours varies somewhat with different sterols, and is orange, carmine red or magenta according to concentration, but all the solutions show selective absorption in the region of $500\mu\mu$. A greenish-blue colour, following a transient pink, is given by ergosterol in dilute solutions (a marked reaction showing even with 0·01 mgrm. in 1 c.c. of chloroform), whilst a yellow colour results when concentrated solutions of ergosterol are used. The latter reaction serves as a useful index for the purity of ergosterol, since oxidised or otherwise changed specimens give, finally, an intense green reaction under the above conditions. A gentian-blue colour is given by products containing vitamin *A* (certain liver oils and the "unsaponifiable" of cod-liver oil). Only those sterols can give colour reactions with nitric acid or with the mercury reagent which possess either the $\Delta^{1,2}$ (or $\Delta^{1,13}$) linkage or the unknown etheroid linkages of the ergosterol molecule. P. H. P.

Conversion of Carotene into Vitamin *A* by Fowls. N. S. Capper, J. M. W. McKibbin and J. H. Prentice. (*Biochem. J.*, 1931, **25**, 265–274.)—It has now been established with a fair degree of certainty by various investigators that carotene possesses vitamin *A* activity; also that, in the rat, carotene is converted into the "classical" vitamin *A* of liver oils. It seemed desirable, before any generalisations could be made, that similar experiments should be carried out with animals differing widely from the rat, and the fowl was chosen for the work which is described. Chickens were successfully reared to maturity on a synthetic vitamin *A*-free diet to which either carotene or cod-liver oil concentrate was added. The carotene was not stored in the liver unchanged, but was converted into vitamin *A* characterised by the blue colour given with antimony trichloride (absorption band 610–630$\mu\mu$), and the presence of an absorption band at $325\mu\mu$. The beaks and shanks of chickens, which had become colourless through the absence of carotenoids from the diet, did not become more yellow when carotene was added to it. The poultry disease, known as visceral gout, would appear to be related to vitamin *A* deficiency, and to be curable by the administration either of carotene or of cod-liver oil. It is shown that the fowl, as well as the rat, can

convert carotene into vitamin *A*; the vitamin *A* requirements of the fowl are higher than those of the rat, weight for weight, and the liver oil of the hen is normally very much richer in vitamin *A* than is cod-liver oil. These experiments support the general theory that, in animals, carotene behaves as a precursor of vitamin *A*. The result of recent work on the relation of carotene to vitamin *A* makes it clear that biological tests alone cannot distinguish between carotene and the "classical" vitamin *A*, and it would seem probable that vitamin *A* is a product of animal synthesis, and ultimately owes its origin entirely to carotene. Land animals can obtain carotene from vegetable matter, and Ahmad (*Biochem. J.*, **1930, 24**, 860) has shown that carotene in diatoms is probably the source of the vitamin *A* of fish-liver oils. P. H. P.

Bacteriological.

Laboratory Tests on the Durability of Philippine Woods against Fungi. O. A. Reinking. (*Philippine J. Sci.*, **1931, 45**, 77–91.)—Results are given of tests made on 15 kinds of Philippine woods and on Southern yellow pine from the United States, using 5 named species of fungi and 9 unnamed cultures of wood-destroying hymenomycetes isolated from various species of local timber. Wide-mouthed 2-litre Erlenmeyer flasks were prepared with layers of culture blocks, $2\times2\times5$ cm., of different non-durable woods, alternated with layers of similar test-blocks of the wood to be examined. Pads of wet cotton-wool were placed at the bottom and top of the pile, and the plugged flasks sterilised and, when cool, inoculated with vigorous bean cultures of the fungi. After the flasks had been kept at room temperature for periods of 7 to 28 months, the character of the fungus growth, the effect on the test and culture blocks, and the weights of the test blocks after oven-drying, were determined.

The loss in weight during 15 months varied from a very small amount to 60 per cent. for the woods examined, and the general order of durability agreed fairly well with published data concerning the service of the woods under practical conditions. It is generally assumed that the resistance of a wood to attack by fungus is determined largely by toxic substances present, but, with highly resinous woods, the action of such substances is undoubtedly supplemented by a water-proofing effect of the resinous materials. The effective toxic constituents in wood vary widely, the tannin groups being important in many species, essential oils in many conifers, and alkaloids in certain other species. T. H. P.

Toxicological and Forensic.

"Ginger Paralysis." (*Brit. Med. J.*, 1931, 322.)—An epidemic of paralysis, which occurred last year in Tennessee as the result of drinking adulterated ginger extract, and was the cause of several deaths, has now been found by the United States Public Health Service to have been caused by tri-ortho-cresyl phosphate, which is used as a cheap adulterant of ginger extract. Physiological experiments

on monkeys showed that the drug was harmless when given by the mouth in large doses, but produced typical paralysis, when injected subcutaneously, both in monkeys and in other animals. Apparently, tricresyl phosphate is not absorbed from the alimentary canal of monkeys, and the erratic incidence of the paralysis in those who drank the adulterated ginger extract points to considerable differences in the extent of its absorption by human beings.

Organic Analysis.

Use of Benzylic Potassium Hydroxide for the Determination of Acetyl Groups in Substituted Acetamides. S. Sabetay and J. Sivadjian. (*J. Pharm. Chim.*, 1931, **123**, 530–531.)—The acetyl groups may be determined in substituted acetamides, such as stovarsol, phenacetin, etc., by adding 25 c.c. of 0·5 *N* benzylic potassium hydroxide to 0·5 to 0·6 grm. of the substances under examination, and boiling under a reflux condenser, together with a blank, for half-an-hour. After cooling, 20 c.c. of neutral ethyl alcohol are added, and the excess of hydroxide is titrated with 0·5 *N* hydrochloric acid, with phenolphthalein as indicator. D. G. H.

Action of Iodine Monochloride on Cholesterol. Determination of the Iodine Value. H. Werner. (*Z. Unters. Lebensm.*, 1931, **61**, 321–337.)—The iodine value of cholesterol was determined under varying experimental conditions by the following methods:—(*a*) Winkler (*id.*, 1922, **43**, 201; ANALYST, 1925, **50**, 523). Bromine is liberated by acidification of a mixture of potassium bromide and bromate. (*b*) Rosenmund and Kuhnhenn's pyridine sulphate dibromide method (*id.*, 1924, **49**, 105). (*c*) Kaufmann (*Z. Unters. Lebensm.*, 1926, **51**, 5). Sodium tribromide is formed by the action of bromine on a saturated solution of sodium bromide in methyl alcohol. (*d*) The Hanus, Hübl and Wijs iodine methods. The results are given in terms of the halogen consumed, expressed as a percentage of the amount theoretically absorbed. They show that the bromimetric methods give more consistent results than the iodimetric methods, (*b*) and (*c*) being preferred, whilst (*c*) has an additional advantage in that the reagent is more stable. For quantities of 0·1 to 0·4 grm. of cholesterol values of 100 per cent. were obtained after 5 to 45 minutes (109 per cent. after 24 hours) with (*b*), and after 20 to 150 minutes with (*c*); (*a*) gave high results. Of the methods (*d*), that of Wijs gave the highest results (*e.g.* 207 per cent. with 0·1 grm. after 15 minutes). It is considered that deviations between the iodimetric methods are greater than would be expected when other unsaturated substances (*e.g.* fats and oils) are used, and are due to substitution of the cholesterol molecule to varying extents by the halogen. The sodium thiosulphate back-titrations were therefore carried out in a neutral medium (carbon tetrachloride), and the halogen acid (H*X*) determined by titration with 0·1 *N* sodium hydroxide solution to phenolphthalein, till a red colour, stable on shaking for 1 minute, was obtained. The acidity (*A*) was then expressed as a percentage of the halogen consumption (*e.g.* according to the general type of reaction $-CH_2-CH_2-+2X \longrightarrow CHX-CH_2-+HX$). The results from the

action of iodine monochloride on cholesterol and dihydrocholesterol and their acetates, and on cholesten and cholestan indicate that substitution, as well as saturation, takes place in the iodimetric methods used for cholesterol, the halogen absorption being relatively small, and A being about 50 per cent. for saturated compounds such as cholestan and dihydrocholesterol acetate. J. G.

New Compounds produced during the Hydrogenation of Fish-Oils. S. Ueno and R. Yamasaki. (*J. Soc. Chem. Ind. Japan*, 1931, **34**, 151B.)—Three kilos. of the evil-smelling volatile matter from a hardened fish oil were shaken with ether and saturated sodium bisulphite, 55 grms. of recrystallised scaly crystals being obtained. On decomposition with sodium carbonate solution and extraction with ether, 22 grms. of a pale yellow liquid were obtained. Most of this distilled at 130–170° C. at 25 mm. pressure, had a solidifying point of −6° C., and contained 78·04 per cent. of carbon and 13·12 per cent. of hydrogen, corresponding with the empirical formula $C_{12}H_{24}O$. Since the melting points of the aldehydes found and their derived acids are much higher than those of the corresponding normal compounds, it was considered that the evil smelling compounds examined were iso-aliphatic aldehydes. R. F. I.

Laboratory Bleaching Technique for Fatty Oils. J. T. R. Andrews and R. G. Folzenlogen. (*J. Oil and Fat Ind.*, 1931, **8**, 183–185.)—In order to put laboratory and works bleaching on to a more comparable basis, it is suggested that the official A.O.C.S. method be modified to include control of the moisture content of the oil. It was found that in the laboratory test on a 300 grm. sample of oil, 3 per cent. of earth with 1 per cent. of water was very nearly equal in bleaching power to 6·0 per cent. of earth without water (the amount recommended in the official laboratory test), and this amount was the optimum. With such moisture control that the added water was about 1 per cent. of the weight of oil taken, laboratory bleaching with English earth was equal to, or better in efficiency than works bleaching. These conclusions were reached from experimental bleaches on works refined cottonseed oil, but some work on refined tallow and coconut oil gave similar results. The optimum moisture for works-scale bleaching is about 0·1 to 0·3 per cent., and under ordinary conditions approximately this amount of water is present. If the laboratory bleaching is carried out below 100° C., no benefit is derived from added water, but from 100° C. improvement is seen up to a maximum at about 135° C. D. G. H.

Fur Dyes, Their Oxidation and Identification on the Fibre. R. B. Forster and C. Soyka. (*J. Soc. Dyers and Col.*, 1931, **47**, 99–109.)—This subject was investigated by Cox (ANALYST, 1929, **54**, 694), whose paper was published while the authors' work was in progress. Two methods, which work well with such skins as rabbit, skunk, sable, beaver, and sheepskins, are now given for the removal of dye bases: (1) Five to ten grms. of the fibre, removed from the pelt, are extracted with petroleum spirit (ligroin) or ether (0·717) in a Soxhlet or indigo extraction apparatus, the extract being evaporated to dryness with 0·5 to 1 c.c.

of *N* hydrochloric acid in a vacuum on a water-bath. The residue is digested with 50 c.c. of 0·1 *N* hydrochloric acid, and the liquid cooled, filtered through several thicknesses of filter-paper to remove the fats, and tested for the bases. (2) The degreased fibre is digested on a water-bath for at least 5 hours with 50 c.c. of 0·1 *N* hydrochloric acid, which is then cooled, filtered, and tested.

If the fur base is present in sufficient quantity, it is sometimes possible to extract and identify it. The hydrochloric acid extract is made alkaline with sodium carbonate in the case of an amine, or neutral in the case of an aminophenol, and extracted with a suitable solvent, *e.g.* benzene or ether (0·717). A number of precipitation and colour tests are given for para- and meta- phenylenediamines, meta-toluylenediamine, ortho-, meta- and para-aminophenols, amidol, metol, pyrogallol, para-aminodimethyl-aniline, 2:4-diaminophenetole, para-aminodiphenylamine, p:p'-diamino-diphenylamine, and Bandrowski's base in various dilutions.

The following are the reactions at dilution of 1:10,000, using (1) aniline hydrochloride and ferric chloride (indamine reaction), (2) nitrous acid, (3) nitrous acid+R-salt, (4) sodium hypochlorite, (5) sodium acetate and *N*/20 diazobenzene chloride, (6) sodium acetate and *N*/20 nitrodiazobenzene chloride:

	1.	2.	3.	4.	5.	6.
p-Phenylenediamine	Green-blue	Very pale yellow	Red	White ppt. yellow solution on boiling	Dirty choc. ppt.	Yellow
m- ,, ,,	Choc. brown at 1:5000	Brown	Pink-brown	White ppt.	Yellow ppt.	Yellow ppt.
m-Toluylenediamine	—	Yellow	Pale scarlet	—	Brown-orange ppt.	Brown-orange ppt.
o-Aminophenol	Red-brown	Greenish-yellow	—	Brown	Brown ppt.	Brown ppt.
m- ,, ,,	—	Colourless	—	—	Yellow ppt.	Yellow ppt.
p- ,, ,,	Pink	Colourless	—	—	Faint brown ppt.	Yellow
Amidol	Cherry red	Orange	—	Orange-yellow	Brown	Brown
Metol	Pink-purple	Colourless	—	Colourless → yellow	Pale yellow	Yellow ppt.
Pyrogallol	Greenish-yellow	Yellow	—	Pale yellow	Yellow ppt.	Yellow
p-Aminodimethylaniline	Pink	Pink-yellow	—	Cherry-red	Cherry-red	Cherry-red-yellow
2:4-Diaminophenetole	Pale pink	Yellow	Cherry-red	Brown-yellow	Orange	Orange
p-Aminodiphenylamine 1:50,000	Pink → brown → green	Orange red	—	Pale yellow	Pink-brown	Pink-brown
pp'-Diaminodiphenylamine	Green-blue	Green	Colourless → blue	Green-blue → pink	Greenish blue	Pale green
Bandrowski's base ..	Brown → green → blue	Brown	—	—	—	—

Details of other dilutions and directions for making up the reagents are given.

Experiments on the oxidation of fur bases on the fibre have been made with meta- and para-phenylenediamines, the oxidation being carried out with hydrogen peroxide in presence of alum-tanned sheepskin, both mordanted and unmordanted. In all cases unoxidised base was found on the fibre, the extent of the oxidation being influenced by the nature of the mordant used and by the *p*H value of the dye liquor. A list of patents (all German) on the use of organic bases for fur dyeing is included. T. H. P.

Determination of Silk in Silk Fabrics. D. Ongaro. (*Giorn. Chim. Ind. Appl.*, 1931, **13**, 159–162.)—The Kjeldahl method is not only lengthy but, when applied to the determination of silk in fabrics, requires the previous removal of nitrogenous dyestuffs. Van Slyke's method gives uncertain results, since the hydrolysis of the silk proteins is influenced by extraneous matters present in the fabrics, and artificial melanins or humin substances are always formed to some extent. The author's results show that the aminic nitrogen of fibroin may be rapidly and accurately determined by oxidising the fibroin by means of alkaline permanganate and ascertaining the amount of ammonia formed. The percentage of nitrogen thus found agreed closely with that of the total nitrogen present. For a series of 10 samples of the fibroin, the ratio between the quantities of aminic nitrogen and total fibroin varied from 1:6·26 to 1:6·32, the mean percentage of aminic nitrogen being thus 15·89.

With a silk fabric, the procedure is as follows:—The fabric is dried at 105–110° C. for two hours or, if very exact results are required, until constant in weight. About 0·3 grm. of the fabric is rapidly weighed in a closed weighing-bottle and transferred to a boiling flask (about 1 litre), where it is boiled until dissolved (a few seconds) with 50 c.c. of 20 per cent. sodium hydroxide solution. Tap-water (150 c.c.) through which air, previously filtered through dilute sulphuric acid, has been passed for 2 hours (this prevents bumping during the subsequent distillation) is then added and the liquid is heated almost to boiling point. About 1 grm. of potassium permanganate per 0·15 grm. of fabric taken is next introduced and the flask is at once connected, through a spray-trap, with a condenser as for a Kjeldahl distillation. The liquid is boiled until it has given about 150 c.c. of distillate, which is collected in 50 c.c. of 0·2 *N* sulphuric acid, the whole being then titrated with 0·2 *N* alkali in presence of methyl red (0·02 grm. dissolved in 100 c.c. of boiling distilled water and the solution filtered). If *A* c.c. of the 0·2 *N* acid have been neutralised by the ammonia distilled over, the weight of pure silk in the fabric taken will be $A \times 0{\cdot}0028016 \times 6{\cdot}292$. T. H. P.

Inorganic Analysis.

Bromimetric Determination of Ammoniacal Nitrogen, I. B. Levy. (*Z. anal. Chem.*, 1931, **84**, 98–106.)—The disadvantages of the determination of ammonia in its salts by oxidation with hypobromite and iodimetric determination

of the excess of this can be avoided if bromine water is substituted for hypobromite and the oxidation is carried out in presence of bicarbonate. The process given, which is suitable for determining from 0·006 to 0·02 grm. of ammonia in the form of any of its ordinary salts, is as follows: To one of two equal portions of the solution are added 15 c.c. of saturated sodium bicarbonate solution, and 0·067 *N* bromine solution (1·8 c.c. of bromine, 120 grms. of potassium bromide, 1 litre of water) is run in until there is an excess of about 4 to 5 c.c., as shown by the yellow colour of the liquid; this gives the approximate quantity of bromine required. For the actual determination, the other portion of the solution, contained in a glass-stoppered flask, is treated with the above quantity of the bromine solution; 15 c.c. of saturated sodium bicarbonate are added, the flask stoppered and kept for 5 minutes; 20 c.c. of potassium iodide solution (5 per cent.) and 20 c.c. of 2 *N* sulphuric acid are added (the latter cautiously down the side of the flask). The solution is kept for 3 to 5 minutes, and the liberated iodine titrated with 0·033 *N* thiosulphate solution, with starch as indicator. The same quantity of bromine solution is standardised by adding the same quantities of reagents and titrating with the thiosulphate. The calculation* of the result can be made from the equation for the oxidation reaction

$$2NH_4X+8NaHCO_3+3Br_2=6NaBr+2NaX+8H_2O+8CO_2+N_2.$$

It is stated that the process can be used for the determination of nitrogen after the Kjeldahl digestion process, the acid being neutralised by sodium bicarbonate.

S. G. C.

* *Note by Abstractor.*—The arithmetical formula given for the calculation is not clear.

Bromimetric Determination of Ammoniacal Nitrogen, II. H. Tschepelewetzky and S. Posdniakowa. (*Z. anal. Chem.*, 1931, **84**, 106–118.)—It is shown that the oxidation of ammonia to nitrogen by bromine is quantitative between *p*H 7·5 and *p*H 9·5, thus confirming Levy's process (*cf.* preceding abstract), in which sodium bicarbonate solution is used as the reaction medium. In strongly alkaline solution some nitrite is formed. In using Levy's process for the analysis of commercial ammonium salts, an addition of some phosphate should be made to prevent the interference, with the iodimetric titration, of any iron which they may contain. These salts may also contain impurities of a reducing nature; it is recommended, if these impurities are suspected, to heat the sample for from 30 to 50 minutes with from 10 to 15 c.c. of concentrated sulphuric acid in a Kjeldahl flask before proceeding with the process. S. G. C.

Determination of Zinc in Cadmium. A. R. Powell. (*J. Inst. Metals*, 1930, **44**, 81–82.)—The metal is dissolved in hydrochloric acid and the solution evaporated nearly to dryness. When cold, it is treated with ammonia (5:1 water) until a clear solution is obtained, and enough solid potassium iodide stirred in to convert the cadmium chloride into iodide (2·5 grms. of potassium iodide per grm. of cadmium) and also to yield a 4 per cent. solution of the precipitant. The white

crystalline precipitate of tetramminecadmium iodide, $Cd(NH_3)_4I_2$, is left to settle, filtered on loose paper, and washed with a 4 per cent. solution of potassium iodide in 80 per cent. ammonia (wash-bottle with Bunsen valve). The excess of ammonia is expelled from the filtrate by evaporation, the acidity of the liquid adjusted to 10 per cent. of hydrochloric acid, and the minute amount of cadmium left in solution precipitated with hydrogen sulphide and filtered off. The zinc in the filtrate is determined by the usual methods (*cf.* ANALYST, 1925, **50**, 18). W. R. S.

Iodimetric Determination of Bromide Ions. Z. Szabo. (*Z. anal. Chem.*, 1931, **84**, 24–30.)—Bromide ions can be oxidised quantitatively to bromate ions by chlorine water in the presence of potassium bicarbonate, provided that a large excess of chlorine is employed. The following process is proposed for the determination of bromide in solution:—To the solution (from 5 to 20 c.c. containing from 0·1 to 20 mgrms. of bromide), contained in a 300 c.c. beaker, are added from 1 to 2 grms. of crystalline potassium bicarbonate and the necessary volume of chlorine water (0·1 mgrm. of bromide requires 30 mgrms. of chlorine, more bromide requires more chlorine up to the 370 mgrms. of chlorine required for 20 mgrms. of bromide). The solution is evaporated practically to dryness. The residue is dissolved in 100 c.c. of water, and 10 c.c. of phenol solution (5 per cent.) are added, with stirring (the phenol is required to remove the last traces of chlorine). After 5 minutes, 1 grm. of potassium iodide is added, the solution is acidified with 25 to 40 c.c. of dilute sulphuric acid (20 per cent.), and, after a further 5 minutes, the liberated iodine is titrated with 0·01 *N* or 0·05 *N* thiosulphate solution, with starch as indicator. The amount of bromide calculated from the thiosulphate used (on the basis of reduction of bromate to bromide) is subject to a slight correction which falls from −0·027 mgrm. (for 0·1 mgrm. found) to zero (for 3·0 mgrm. found), rising proportionately to +0·37 mgrm. (for 20·0 mgrm. found). Any iodide present with the bromide to be determined must be removed by acidifying the solution with sulphuric acid and boiling after addition of potassium nitrite. No reference is made to the determination of bromide in the presence of chloride. S. G. C.

Volumetric Determination and Separation of Ortho-, Pyro-, and Metaphosphoric Acids. S. Aoyana. (*Z. anal. Chem.*, 1931, **84**, 31–35.)—The author has revised his earlier process (*J. Pharm. Soc. Japan*, 1925, No. **520**, 553; *Bull. Imperial Hygienic Laboratories*, 1926, **27**, 131), and now proposes the following method in which the solution, rendered slightly alkaline to phenolphthalein, is precipitated with silver nitrate, and the acid liberated (according to the equation $Na_2HPO_4+3AgNO_3=Ag_3PO_4+2NaNO_3+HNO_3$) neutralised with borax; the excess of silver in the solution is titrated, whence the amount of silver equivalent to the total phosphate is obtained; the precipitate of silver phosphate is decomposed with hydrogen sulphide and the liberated phosphoric acid is titrated with alkali to methyl orange and also to phenolphthalein; the amount of the three phosphoric acids can then be calculated. *Method*:—To two equal portions of the solution containing the mixture of ortho-, pyro-, and metaphosphoric acids or their alkali

salts, in amount approximately equivalent to from 10 to 20 c.c. of 0·1 *N* silver nitrate solution, is added 0·1 *N* alkali until the solution reacts slightly alkaline to phenolphthalein. A preliminary trial is now made by adding to one portion 25 c.c. of 0·1 *N* silver nitrate solution and titrating with 0·1 *M* borax solution, the amount of the latter required to render the solution slightly alkaline to litmus paper being noted. To the other portion are added 25 c.c. of 0·1 *N* silver nitrate solution, followed by 0·05 c.c. less than the quantity of borax solution previously found, and the solution is diluted with an equal volume of alcohol. The solution is filtered, the precipitate washed with 50 per cent. alcohol, and the filtrate is diluted with an equal volume of water and its silver content titrated by the Volhard method; the difference between this amount of silver (expressed as c.c. of 0·1 *N* silver nitrate solution) and the amount initially added is called *a*. The filter carrying the precipitate of silver phosphate is placed in a flask together with not more than 30 c.c. of water, and hydrogen sulphide passed into it for 15 minutes; the liquid is filtered into a flask, the filter being washed until the runnings are neutral. The filtrate is evaporated to 30 c.c. under reduced pressure at a temperature below 40° C., transferred to a beaker with not more than 20 c.c. of water, 45 c.c. of saturated sodium chloride solution are added, and the liquid is titrated with 0·1 *N* alkali to methyl orange; the volume of alkali solution used is called *b*. Finally, a further 55 c.c. of saturated sodium chloride solution are added to this same liquid, and the titration with alkali continued until the end-point to phenolphthalein is reached; the total number of c.c. of 0·1 *N* alkali thus used is called *c* (a "blank" titration of 55 c.c. of the sodium chloride solution with the alkali, to phenolphthalein, is deducted from *c*). The amounts of ortho-, pyro-, and metaphosphoric acids can be calculated from the following:

$$3x+4y+z=a;\quad x+2y+z=b;\quad 2x+4y+z=c;$$

where x represents the number of c.c. of 0·1 *N* orthophosphoric acid; y of pyrophosphoric acid; and z of metaphosphoric acid. S. G. C.

New Method for Dissolving Cassiterite. S. Tamaru and N. Ando. (*Z. anal. Chem.*, 1931, **84**, 89–98.)—Many attempts are described in which finely-ground mixtures of cassiterite, lime and carbon are heated with a view to finding a method of treatment of cassiterite which would yield the tin in a form soluble in hydrochloric acid. In the experiments in which crucibles were used for the heating, more or less of the tin always remained insoluble. The only successful experiment, in which all the tin was ultimately obtained in solution, was one in which 0·3 grm. of cassiterite, 0·78 grm. of lime and 0·0138 grm. of charcoal (0·0126 grm. of carbon was required to combine with the oxygen in the tube used) were placed in a boat which was heated in the closed end of a quartz tube (36 cm. long, 2·1 cm. diameter, 120 c.c. volume) at 900° C. for 1 hour; the free end of the tube projected from the furnace and was closed by a rubber stopper. After the heating, the product had a sintered appearance and dissolved completely in dilute hydrochloric acid (1:1). It is stated (without any supporting data) that, in the reduction of cassiterite by heating with potassium cyanide, some tin is lost by volatilisation of stannous oxide. S. G. C.

Measurement of Hydroxyl and Hydrosulphide Ions in Sodium Sulphide Solutions. A. W. Goetz. (*J. Amer. Leather Chem. Assoc.*, **1931**, **26**, 234.)—The hydrogen electrode being unreliable in the presence of sulphides, the use of the antimony electrode is recommended. It is, however, essential to standardise its form. An antimony rod, 5 inches long and $\frac{1}{4}$ inch in diameter, cast in a hot mould, quenched and surface-polished, was found best from the point of view of time and stability. The E.M.F. values for sodium sulphide, sodium hydrosulphide, sodium hydroxide, and sodium carbonate, as found by the antimony electrode, are plotted against the logs of their respective dilutions. To obtain the *p*H values corresponding with the E.M.F. values as found by the antimony electrode, the cube roots of the sodium hydroxide normalities were plotted against the corresponding OH-ion concentration. Then the OH-ion concentration for any sodium hydroxide normality being known, and its corresponding E.M.F., the OH-ion concentrations of solutions of the above salts can be obtained from the graph (log OH-ion concentration against the E.M.F. of sodium hydroxide taken with the antimony electrode).

The *p*H values at decinormal concentration are found to be as follows:—Na_2S, 13·86; NaOH, 12·96; Na_2CO_3, 11·09.

The E.M.F. changes of both the antimony and the mercury and mercury sulphide electrodes with sodium sulphide solutions from 0·1 *N* to 1·0 *N* closely approximate to the Nernst equation $E = RT/F \ln (H)^+$ R. F. I.

Microchemical.

Quinoline as a Microchemical Reagent for some of the Heavy Metals. J. M. Kovenman. (*Mikrochem.*, **1931**, **9**, 223–228.)—Many salts of the heavy metals give sparingly soluble complex or double salts with quinoline in the presence of halogen salts. The sensitiveness of the reactions used as tests depends on the order of mixing the various reagents. The usual procedure is to mix a drop of quinoline or quinoline hydrochloride with a drop of saturated potassium iodide solution, and then to add a drop of the acid solution under examination. *Bismuth* gives a dark brown or orange-yellow precipitate seen under the microscope as crosses, rectangles and parallelograms; 0·1–0·2γ of bismuth may be detected. *Antimony* salts give similar crystals; 0·2–0·3γ of antimony is detectable. *Tin* reacts only in more concentrated solutions (1:300 or 1:500), 3γ being detectable; the crystals are seen as long yellow needles and parallelograms. *Mercuric* chloride reacts in neutral solution, and, after rubbing with a glass rod, the crystals are seen as colourless needles and rosettes; 0·25 to 0·3γ of mercury is detectable. The reaction is slightly less sensitive in hydrochloric acid solution, and less sensitive still in nitric acid solution. *Cadmium* salts alone in acetic acid or sulphuric acid solution give no precipitate with quinoline, but do so when potassium iodide (or other halogen salt) is also present, when 0·15–0·1γ of cadmium is detectable. The crystals appear as fine needles under the microscope. *Copper* salts in 1:100 to 1:200 dilution give an amorphous precipitate with quinoline. In the presence of potassium iodide the reaction is more sensitive and is characteristic. In acid

solution a dark brown crystalline precipitate is formed, appearing as rhomboids and octagons under the microscope; 0·15 to 0·2γ of copper is detectable. When ammonium thiocyanate is used instead of potassium iodide in the test for copper a green crystalline precipitate is formed; in neutral solution 0·15γ of copper is detectable. Under the same conditions cadmium gives colourless crystals appearing as rectangles or parallelograms, and 1γ of cadmium is detectable. *Zinc* salts give a characteristic reaction with quinoline and potassium bromide. Large rhomboidal crystals are formed, and 0·5 to 0·6γ of zinc is detectable. Mercuric chloride gives somewhat similar crystals under the same conditions, but, unlike the zinc compound, the mercuric compound is soluble in excess of the reagent. *Lead* salts give a crystalline precipitate with quinoline and potassium iodide, and 0·1γ of lead is detectable. The reaction is less sensitive in neutral solution than in acid solution. In the presence of a small amount of an oxidising agent the acid reagent forms a sparingly soluble quinoline periodide, which is seen as long needle-shaped blue-green crystals. This reaction is used as a test for dichromates. A reagent for testing for iron, zinc, cobalt and cadmium salts is prepared from equal parts of quinoline and ammonium thiocyanate, to which dilute nitric acid is added, drop by drop, until the quinoline dissolves. With *iron* salts the reagent forms red crystals of varied form, and 0·3γ of iron is detectable. *Zinc* salts give colourless rhombs and hexagons, but the reaction is not very sensitive. *Cobalt* salts give blue crystals of varied forms. *Cadmium* gives the most characteristic reaction, the crystals being formed in bushy groups; 3γ of cadmium is detectable. The reagent must be freshly prepared or crystals of $C_9H_7N.HCSN$ are formed and interfere with the tests. Drawings of the various crystals are given in the original. J. W. B.

Systematic Qualitative Analysis by means of Modern Drop Reactions. C. J. van Nieuwenburg. (*Mikrochem.*, 1931, **9**, 199.)—A systematic qualitative analysis (which has been used by the students in Delft University for a year) combines some of the older group separations with the modern drop or "spot" tests as identification reactions. Only half the time is required for an analysis, and the results are better. The system is devised for the analysis of any mixture of the following cations:—Ag, $Hg_2^{\cdot\cdot}$, As, Sb, Sn, $Hg^{\cdot\cdot}$, Pb, Cu, Cd, Bi, Al, Cr, Te, U, Ni, Co, Mn, Zn, Mg, Ba, Sr, Ca, K, Na, and $NH_4^{\cdot}$; and the anions: Cl′, Br′, I′, CN′, CNS′, SO_4'', SiF_6'', NO_2', NO_3', HCOO′, CH_3COO', SO_3'', S_2O_3'', S″, CO_3'', BO_2', PO_4''', and SiO_3. The amount of sample used is 50 to 200 mgrms. The preliminary examination by the dry method is retained. In the group precipitated with hydrogen sulphide the sulphides of arsenic, antimony and tin are dissolved in 2 *N* potassium hydroxide (in which, contrary to expectation, mercuric sulphide is practically insoluble), after stannous salts have been oxidised to the stannic condition with bromine water. The hydroxides of aluminium, chromium, iron and uranium form the next group, and cobalt, nickel, manganese, and zinc are then precipitated with ammonium sulphide together. Magnesium is grouped with the alkaline earths by gently heating with ammonium carbonate,

after expelling the excess of ammonium salts, the alkalis remaining together in solution. The final identification tests can be carried out on a drop of the solution as follows:—*Silver*, with a solution of rhodanine (dimethyl-amino-benzylidene-rhodanine) gives a red colour, whilst mercury does not react in the presence of potassium cyanide. *Mercury* gives an intense blue colour with an alcoholic solution of diphenylcarbazide. The mercury solution should be neutralised with potassium hydroxide, but should not be alkaline. *Lead* hydroxide is oxidised to lead peroxide with alkaline hydrogen peroxide, which should then be removed, and the lead peroxide is detected by the blue colour with tetra-methyl-diamino-diphenyl-methane. Bismuth must first be removed by extraction with sulphuric acid. *Bismuth* is identified by catalysing the reduction of lead acetate by potassium stannate. *Copper* is identified by the formation of blue-violet crystals on adding zinc sulphate and ammonium-mercury thiocyanate. *Cadmium* is identified by the formation of the metal by heating with sodium carbonate and charcoal in a capillary tube, and the subsequent formation of the sulphide with sulphur. For *arsenic* the Gutzeit reaction is used. *Antimony* is reduced with tin in hydrochloric acid, or, better, is identified by means of rhodamine B, after oxidation with solid sodium nitrite (Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*). *Tin* in the stannous state turns the yellow colour of a dilute solution of cacotheline, a nitration product of brucine (Dryer, *Chem. News*, **1883**, **48**, 257), brown-violet. *Aluminium* gives a red stain on filter paper impregnated with alizarine S; this is developed over ammonia fumes and is not affected by a large excess of $N/5$ acetic acid, but ferric salts interfere. For *iron* the usual thiocyanate test is used *Chromium* is converted into the chromate, which in acid solution gives a bright violet colour with diphenylcarbazide solution. *Uranium* is detected by the usual ferrocyanide reaction. *Cobalt* solutions with three volumes of ethyl alcohol and some crystals of solid ammonium cyanide give an intense blue colour. Interference of iron is prevented by the use of tartaric acid. A second test is the red-brown stain on filter paper with α-nitroso-β-naphthol, which (unlike the iron and nickel colorations) is not affected by 2 N hydrochloric acid. *Nickel* gives a red precipitate with dimethylglyoxime in slightly ammoniacal solution, or (in the presence of cobalt) tartaric acid solution, when hydrogen peroxide and finally solid sodium carbonate are added. *Manganese* with benzidine acetate in the presence of dilute acetic acid gives a bright blue colour. When cobalt is present tartaric acid, or a tartrate must be added. Marshall and Walter's reaction (*Chem. News*, 1901, **83**, 76; **84**, 239), using phosphoric acid instead of sulphuric acid for the formation of permanganate, is also used. For *zinc* the same reaction as for copper is used. A suspension of *magnesium* hydroxide, carbonate or phosphate in an alkaline liquid, boiled with a few drops of Titan yellow (azidine yellow, 5G) is coloured violet-red. The ordinary macro-chemical separation is used for calcium, barium and strontium. *Potassium* is identified by the cobaltinitrite reaction, *sodium* with zinc uranyl acetate, and *ammonium* in the usual way. The old tests are used for all the anions except silicates, fluorides and sulphides, for which Feigl's tests are used. Solid *sulphides* catalytically accelerate the reaction of a dilute solution of sodium

azide with a solution of iodine in potassium iodide solution, when nitrogen is vigorously evolved. Soluble *silicic acid* is boiled with a few crystals of ammonium molybdate and a few drops of dilute nitric acid; on cooling, a few drops of benzidine acetate and solid sodium acetate are added, and a blue colour indicates silicic acid. Phosphoric acid also reacts, and chlorides interfere with the reaction. For mineral silicic acid the substance is heated with a little solid fluoride and a few drops of concentrated sulphuric acid in a lead crucible, covered with a cellon plate on which is hanging a drop of water. The water reacts with the silicon fluoride, which is converted into soluble silicic acid which can then be tested as before. *Fluorides* are similarly identified by heating with ground quartz in the lead crucible and then testing for silicic acid in the drop. Fluorides not decomposed by sulphuric acid must first be fused with solid sodium hydroxide. J. W. B.

Detection of Gold, Palladium and Silver with Dimethylamino-benzylidene Rhodanine. F. Feigl, P. Krumholz and E. Rajmann. (*Mikrochem.*, 1931, **9**, 165–173.)—Rhodanine was first used by Feigl (ANALYST, 1928, **53**, 615) as a reagent for silver and mercury. As other precious metals also react, giving coloured products with the reagent, the procedure must be varied according to the metal that is to be detected. The tests may be carried out in a test tube, when the coloured product is extracted with a few drops of ether, and is clearly seen on the boundary of the two liquids, or else as "spot" tests, using either a "spot" plate or filter paper impregnated with the reagent, and then dried. 1. *Detection of silver in the presence of gold, platinum and palladium.*—A drop of the test solution is mixed on a spot plate with a drop of 10 per cent. potassium cyanide solution, and then a drop of the alcoholic solution of *p*-dimethylamino-benzylidene-rhodanine is added and acidified with a few drops of *N* nitric acid, when the silver cyanide gives a violet colour with the rhodanine. As little as 1γ silver in the presence of 1000γ of mercury, 4000γ of gold or 300γ of palladium or platinum may be detected; the limit of dilution of silver is 1:50,000. Copper should not be present. 2. *Detection of gold.*—Gold salts give a red-violet precipitate with rhodanine in neutral and slightly acid solutions. The smallest amount detectable is 4γ of gold in a concentration 1:500,000 in 0·1 *N* hydrochloric acid solution when the test is carried out in a small test tube. As a "spot" test on paper, the smallest amount detectable is 0·1γ of gold, in the same dilution. *Detection of palladium in the presence of other metals.*—Platinum reacts slowly with the reagent (only as $Pt^{\cdot\cdot}$), so that when the test is carried out on impregnated filter paper the violet coloration due to palladium is visible almost immediately, and the coloration due to platinum is formed later in the zone outside, owing to diffusion through the capillaries of the paper. In this way 0·038γ of palladium can be detected in the presence of 20,000 times the amount of platinum. In the presence of gold or iridium the solution is boiled before the test with an alkali nitrite in the presence of excess of calcium carbonate, when both metals are precipitated, but the palladium remains unchanged. Osmium, rhodium and ruthenium salts give no reaction in 0·05 to 0·1 per cent. solutions, so that, after suitable dilution, these metals do not interfere.

When silver is present it is made inactive by the formation of the complex salt $K[AgBr_2]$, by treating the test solution with excess of solid potassium bromide. When the test is carried out in a test tube 1γ of palladium can be detected in the presence of $10{,}000\gamma$ of silver in a dilution 1:1 million. When carried out as a "spot" test $0{\cdot}05\gamma$ of palladium can be detected in the presence of 1000 times the amount of silver in the same dilution. J. W. B.

Determination of Potassium in Dilute Solutions. M. Wrangel. (*Z. anal. Chem.*, 1930, **82**, 224–230.)—Potassium is precipitated as the cobaltinitrite, in which the nitrous acid is determined colorimetrically with indol sulphonic acid. The method is used for the analysis of soil solutions, and is suitable for determining from 0·02 to 0·06 mgrm. of K_2O, with an error of 0·2 per cent. For each analysis 20 c.c. of soil solution are evaporated to dryness in a quartz dish, and then gently heated to drive off the ammonium salts. The cold residue is dissolved in exactly 2 c.c. of 3 per cent. acetic acid, and 1 c.c. of the solution is pipetted into a centrifuge tube, and 1 c.c. of Tisdall and Kramer's (*J. Biol. Chem.*, 1921, **46**, 339) cobaltinitrite reagent is added, and the mixture is left for at least 3 hours. It is then centrifuged for 20 minutes, and after removing the supernatant liquid, it is washed and centrifuged thrice, each time with 2 c.c. of water. The precipitate is dissolved by gently heating with 5 c.c. of 0·1 *N* sodium hydroxide, and the solution is transferred to a 100 c.c. measuring cylinder. After diluting to 98 c.c., 1 c.c. of indol solution (0·15 grm. of indol dissolved in 10 c.c. of alcohol, and diluted to 100 c.c. with water) and 1 c.c. of sulphuric acid (1:1) are added. The maximum carmine-red colour is reached after 5 or 10 minutes. The standard solution contains sodium nitrite equivalent to 0·005 mgrm. of K_2O per c.c. It is prepared from 0·4902 grm. of silver nitrite and sodium chloride. The filtrate is diluted to 1 litre, and diluted a further ten times before use. Potash-free glass should be used. J. W. B.

Reviews.

REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. XV for 1930. Issued by the Society of Chemical Industry. Pp. 745. Price, post free, 7s. 6d. to members, 12s. 6d. to non-members, of the Society.

Unlike the Annual Reports on the Progress of Chemistry, issued by the Chemical Society of London, the volume under review contains no special chapter on analytical chemistry. This branch is, however, by no means neglected, and, in a number of the articles, is considered under a separate heading.

As is bound to be the case in a compilation of this kind, in which different subjects are reported by different authors, there is some unevenness in the manner of treatment adopted. This is particularly noticeable when the chapters on the fermentation industries and foods, respectively, are compared. Each of these

chapters forms a most readable and complete contribution, but the former is written in discursive fashion and occupies 40 pages, whereas the report on foods is only just over one-half as long. It may be that, in order to keep the size and cost of the book within reasonable limits, each subject is allotted a certain space, but many members of our own Society would doubtless like to have a little more room found for an all-important matter like foods.

The effects on industry of the world-wide economic depression of 1930, with the accompanying general drop in the prices of commodities, are discussed by a number of the contributors. In some sections such effects have been severely felt, although, on the whole, the chemical industry does not appear to have suffered so badly as certain others.

Perusal of this volume indicates no slackening in the efforts to improve plant and processes or to discover new uses for chemical products. Under "General, Plant, and Machinery," reference is made to the principal developments in the fixed nitrogen and other chemical industries at home and abroad, and to work on heat transfer, general plant operations and equipment, etc. The chapter on "Fuel" deals with economic problems such as scientific marketing, and with carbonisation, coke ovens, coal cleaning, and gaseous fuel. A number of investigations on the origin and composition of coal are described, the growing opinion that coal is derived mainly from the lignin, and not from the cellulose of the original plant material, being expressed. The question of atmospheric pollution is considered, and a section on the analysis and testing of fuels is included. In the chapter on gas, tar, etc., the stability and prosperity of the gas industry are indicated, and the examination of gas and of the bye-products of the industry is discussed.

The section on mineral oils deals at length with the important developments made in connection with hydrogenation, cracking, and the manufacture of intermediates from petroleum. Fewer special results than usual are recorded under "Colouring Matters and Dyes," although the volume of research work did not fall below that of recent years; it is gratifying to note the increasing proportion of inventions patented by British manufacturers. In the textile industries, the most noteworthy advances made during 1930 have been, not through new discoveries and inventions, but rather in the way of economics and trade organisation. As regards bleaching, dyeing, printing, and finishing, research has been devoted mainly to artificial silk, and, owing largely to the efforts of the English textile research associations, such research in this country has been more intensive than, and ahead of, that on the Continent. Much interesting work, but nothing of outstanding moment, is noticed under "Acids, Alkalis, and Salts, etc.," "Refractories, Ceramics, and Cements," "Iron and Steel," "Non-Ferrous Metals," and "Electro-Chemical and Electro-Metallurgical Industries." Under "Glass" are given references to various methods for the analysis of silicates and glass-making materials. Under specified conditions, 8-hydroxyquinoline has been found a good precipitant for separating alumina from molybdenum, uranium,

vanadium, arsenic, and fluorine; a rapid modification of the Berzelius method of determining fluorine, and a microchemical procedure for analysing as little as 0·01 grm. of glass are described.

"Oils, Fats, and Waxes" includes copious references to the fundamental investigations of Hilditch and his collaborators, and reports various testing and analytical methods. Carbon disulphide and sulphur may be detected by treating a chloroform solution of the oil with a copper salt and hydroxylamine hydrochloride, a chocolate-coloured solution and precipitate being formed. The Committee of the Society of Leather Trades' Chemists has decided in favour of the Hanus method of determining iodine values. Work on "Resins and Solvents" has been concerned largely with synthetic products, and under "Cellulose Ester Varnishes and Enamels" attention is drawn to the increasing use of compounds of the more complicated mixed types. The position of rubber, a commodity dependent, for its consumption, almost entirely on the tyre manufacturer, is adequately discussed, and a considerable volume of research recorded. With regard to "Leather and Glue," much work has been expended on the preservation of hides and skins, on the sterilisation of anthrax-infected hides, as well as on tannery operations and materials generally. Although no marked changes have been made in the analysis of vegetable-tanned leather during the present century, recommendations have now been made by a committee of the Society of Leather Trades' Chemists for the standardisation of the procedure involved in such analysis.

The salient feature of the article on "Soils and Fertilisers" is the marked interest shown in the Russian work on the morphology and genetic classification of soils, which is now becoming better understood in other countries. Important results following on the application of *X*-ray analysis to clays are noted, and reveal the possibility of establishing characteristic micro-crystals in soil clay. The suitability of bromocresol green as an indicator for Kjeldahl titrations is pointed out, and various methods for determining citric-soluble phosphoric acid are given. The high proportions of sucrose indicated in French beets of the 1929–1930 campaign by the direct polarisation method are ascribed to the presence of raffinose and nitrogenous substances, although another opinion is that pectic substances, more easily dissolved by the hot aqueous digestion of the analytical method than in the technical diffusion, caused the high results. Valuable information is obtainable by the "polarographic" method of examining sugar, the presence of molasses at 0·00002 per cent. concentration in 5 per cent. sucrose solution being detectable. In the chapter on "The Fermentation Industries," the examination of vinegar is considered, and methods of determining the dry extract and of distinguishing between different grades of wine vinegar and synthetic and distilled vinegars are reported.

Under the heading "Foods," attention is drawn to the continued interest in examination for vitamin contents. A large amount of work has been carried out on milk and dairy products. Further results go to establish the value of the freezing point in the detection of adulteration of milk, and it has been found that the difference

between the values for genuine and watered fresh milks is maintained if the milks acidify spontaneously to the same (but not too marked) extent. Analysis of numerous normal milks confirms the substantial accuracy of the Vieth ratio, lactose: protein: ash = 13 : 9 : 2, these figures holding also for condensed and dried milks. The compressibility of the crumb has been suggested as a measure of the staleness of bread, and the retardation of staling by the action of aldehydes is regarded as due to combination of the aldehyde with the albumins present. The acidity of flour, for which a limiting value is included in the Greek Government specification, is discussed. The examination of foodstuffs for preservatives has come in for a good deal of attention. The determination of boric acid has been exhaustively considered in THE ANALYST, and the use of benzidine in preference to iodine has been suggested for determining sulphur dioxide, for which also a simplification of the Monier-Williams method has been proposed. A useful review of the literature dealing with the preservation of food is noted. Diverse opinions exist concerning the value of formol titration for detecting adulteration of honey with artificial invert sugar, and the value of a determination of hydroxymethylfurfuraldehyde for this purpose has been considered. Incipient putrefaction in meat and fish may be judged from the content of ammonium salts, the critical value being about 0·02 per cent. as NH_3. The pH value appears to be of little value for fixing the age of eggs, as, for the white, it increases from 7·6 to 9·0 in 7 days, and then remains unchanged, whereas, for the yolk, it alters from 6·0 to only 6·2 during 10 weeks. Relatively large amounts of aluminium appear to be innocuous to the animal organism, and the quantities of aluminium dissolved from cooking vessels of this metal to be devoid of physiological significance. Examination of the semi-carbazones has been found of value in the identification of the components of flavouring materials.

Under "Sanitation and Water Purification," emphasis is laid on the increased efforts necessary to deal effectively with sewage and trade effluents owing to the growth of the population and the development of industry. Chapters on "Fine Chemicals, Medicinal Substances, and Essential Oils," "Photographic Materials and Processes," and "Explosives" are followed by Name and Subject Indexes.

These Annual Reports, which must surely be among the cheapest scientific publications in the English language, are known so well that no recommendation is needed. It may, however, be stated that Volume XV is well up to the standard of its predecessors. Few errors, even in spelling, are noticeable, but "Wedgewood" is given twice in the text, although the index has it "Wedgwood."

T. H. POPE.

THE CHEMICAL INVESTIGATION OF PLANTS. L. ROSENTHALER. Translated from the 3rd German Edition by SUDHAMOY GHOSH. London: Bell & Sons. 1930. Price 12s. 6d.

This translation of Dr. Rosenthaler's well-known treatise will be welcomed by all who are interested in the analysis of plant products. A short historical introduction, very unequal in its treatment of the various groups, opens the general

section. This includes preliminary qualitative tests for the most important groups of compounds, and some account of the methods of extraction and separation. From the point of view of logical arrangement it is a pity that these two chapters are separated by chapters dealing with alkaloids and glucosides, which might more appropriately have found a place elsewhere.

The bulk of the book is occupied by the special section, the 19 chapters of which deal with fats, waxes, resins, proteins, etc. These contain a great deal of useful matter, but here, again, the treatment must be regarded as unequal. The chapter on organic acids is adequate, and the reference to the microchemical methods of Klein and Werner is welcome. Resins, alkaloids and glucosides also receive fairly full treatment. The qualitative part of the chapter on carbohydrates is full, but less than a page is devoted to the estimation of sugars. The chapter on colouring matters opens with the statement, "The majority of the colouring substances occur as glucosides," and only the anthocyans are dealt with.

Several omissions have been noted. In connection with the fats a series of 12 colour tests is given without mention either of the results or of the conclusions to be drawn. The convenient benzidine test finds no place in the list of oxidase reagents. No mention is made of the goldbeater's skin test for tannins. Lichenin is said to give a blue coloration with iodine.

In addition to references in the body of the work a bibliographical appendix with 177 entries is provided; of these, only 7 refer to sources in English. It is a serious fault that no reference is made to such important English books as Onslow's "Anthocyans," Osborne's "Vegetable Proteins," and Carré's "Pectic Substances." It is to be presumed that workers who require to use a translation of Dr. Rosenthaler's book would prefer to be guided to further details in their own language where these are available. M. SKENE.

BIOASSAYS. A HANDBOOK OF QUANTITATIVE PHARMACOLOGY. By JAMES C. MUNCH. Pp. x+958. London: Baillière, Tindall & Cox. 1931. Price 45s.

The word "bioassay" is a new one; and although it is certainly less unwieldy than the terms in general use, "physiological assay" and "assay by a biological method," it is doubtful whether it can rightly be regarded as synonymous with the sub-title of this book, "A Handbook of Quantitative Pharmacology."

The present volume comprises a much wider field than that implied by the title. It is a compilation of general information and of the results of research relating to physiological testing. It includes much chemistry and pharmacology. The task which the author undertook was one demanding very great perseverance and the expenditure of much time. Over 17,000 references have been tabulated; briefly to consult and abstract a large proportion of these original communications alone has required an immense amount of application. It should be added here that the bibliography, given as an appendix to successive chapters, constitutes a valuable and important feature. It occupies about one-quarter of the text, some 230 pages in all.

The first three chapters deal successively with the general subject of physiological assays, the experimental technique, and the interpretation of results. In the six chapters which follow, drugs are roughly classified according to their action, those that act upon the nervous, circulatory, respiratory and muscular systems being treated separately. One chapter is given to hormones, and another to special types of drugs, and vitamins.

As a compilation of classified observations relating to quantitative pharmacology, the volume will prove invaluable to those who require a ready book of reference relating to this field of knowledge. On the other hand, those needing guidance in the choice of a biological method of assay will wish that the author had made freer use of his critical faculty in selecting that which is likely to prove of practical value, and omitting much which is not. By adopting this course, he would have given the reader who wishes to carry out physiological assays greater help in choosing the methods suited to his needs. Indeed, the book is more in the nature of a general textbook than of one dealing with methods of analysis.

Those unacquainted with the present state of our knowledge must not suppose it to be possible in more than a few instances to undertake true quantitative evaluation of active principles by biological methods. The title might lead one to hope for a collection of select methods of analysis giving a detailed description of the best procedure. The book contains very little that comes up to such expectations, and, if truth be said, accurate biological methods of assay are of too recent introduction to make possible a textbook of select methods of assay relating to more than a few substances.

The book is a truly useful one, dealing with the steps that have been taken towards the evolution of satisfactory methods of assay. It is well produced, and contains a number of useful figures and plates, and some 240 tables of classified information. To one wishing to commence research in this field, it will be found to be teeming with suggestions, for it shows only too clearly that our knowledge of pharmacology, although so extensive, is still in a very elementary state.

F. H. CARR.

THE VITAMINS. By H. C. SHERMAN and S. L. SMITH. An American Chemical Society Monograph. Second Edition. New York: The Chemical Catalog Company, Inc. 1931. Price $6.00.

The first edition of this book was published in 1922. It was obvious at once that further editions would be called for as knowledge of the vitamins became extended. The second edition fulfils the promise of the first, and all the more important researches on the subject published before the middle of 1930 have been considered. This has involved the re-writing of large sections of the book in order to get relevant facts in their right relationship; the new facts have not merely been added at the ends of the appropriate chapters.

The book has singularly few mis-statements and mis-interpretations, but the account of one investigation is inaccurate, and may be misleading when, for practical reasons, it is essential that there should be no misunderstanding. Hess

and Weinstock are reported as having conferred antirachitic potency on certain foodstuffs by ultra-violet irradiation in 1924 and 1925, whereas Steenbock and Black are reported as having achieved this result in 1925. Actually Steenbock's first work on this subject was published in 1924, some months before Hess published any work on it. The paper in which Steenbock described this work is cited in the bibliography.

It is regrettable, also, that Sherman and Smith have retained and used so extensively the definition for a "unit of vitamin *A*" which was proposed originally by them, and which was later adopted by the United States Pharmacopoeia, for so many workers have pointed out the possibility of variation in the value of this "unit" that it seems to be impossible to accept it for general use.

The book is remarkable also for its bibliography which occupies some 180 pages, about one-third of the total number. Vitamin workers will be grateful to the authors for the care with which this has been compiled. Indeed, the whole book forms a valuable work of reference, a copy of which every serious worker on the subject will wish to possess. KATHARINE H. COWARD.

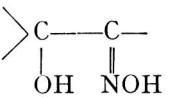
QUALITATIVE ANALYSE MIT HILFE VON TÜPFELREAKTIONEN. By Dr. FRITZ FEIGL. Pp. viii+387, with 12 figures in the text and 2 coloured plates. Leipzig: Akademische Verlags-gesellschaft M.B.H. 1931. Stitched R.M. 26.40; bound R.M. 28.

Dr. Feigl is the leading authority on the "spot" or "drop" test method of qualitative micro-analysis, in which a drop of solution (0·05 c.c.) is used for each test, and the reactions usually involve a colour change, either of the solution or by the formation of a coloured precipitate. The simplicity of most of the tests, and the rapidity with which they can be carried out, account for their increasing popularity, not only in the realms where micro-technique is essential, but also as an alternative to ordinary macro-procedure. Dr. Feigl's book is, therefore, particularly useful, in that it is the first book to cover the whole range of "spot" tests, not only with careful detail on the practical side, but also with considerable attention to all the underlying theory.

Most of the tests involve the use of organic reagents, many of which, in controlled conditions, give specific reactions with certain inorganic ions. The number of organic reagents is continually being augmented, and there is still a large field for research, since slight changes in the organic radicle may cause changes in the intensity of colour and solubility of the reaction produced. An advantage of organic reagents is that the large molecule often increases the visibility of the reaction product, and so decreases the amount recognisable by the test. Many tests may be rendered more sensitive by the use of an organic reagent—an example is the precipitation of magnesium as the hydroxide which is a very insensitive test, but in the presence of an organic dye stuff (*p*-nitrobenzene-azo-*α*-naphthol) which adsorbs magnesium hydroxide, as little as 0·24γ of magnesia in a dilution of 1 in 4 millions can be detected.

The presence of other substances may influence a reaction considerably, and

may sometimes completely mask it. Dr. Feigl, therefore, describes very thoroughly the theory of "masked" reactions, as well as the opposite effect, when the presence of other ions increases the sensitiveness of a test, and gives some well-chosen examples. There is a chapter on the theories and types of the different complex salts, as formed in "spot" tests, and the organic groups with specific reactions for certain inorganic ions, such as the NH-group for silver, and the



radicle for copper, are described in detail. There is an important chapter on the effect of various changes in grouping on the solubility of the reaction product in various solvents. The theoretical section ends with a chapter on capillarity as it applies to "spot" tests, for many tests are carried out on filter paper, when the capillaries of the filter paper play an important part.

The practical section of the book consists in descriptions of the tests for all the different inorganic ions, with full experimental details, which even include the method of preparation of the reagent when it is rare. Where a test is modified or masked by the presence of other ions, particulars are given. The smallest amount recognisable, and the limit of dilution, which are the terms always used by the author to define the sensitiveness of a test, are given for every test, and must have involved a large amount of work, since about 160 tests are given. Several methods have been devised for the systematic analysis of mixtures by the "spot" method, and the author describes four of these in detail.

The book ends with a number of valuable descriptions of the analytical procedure in the investigation of a number of special substances. The descriptions include tests for the purity of certain compounds, tests for copper in alloys, for lead in enamels, chromium in minerals, for mineral salts used in the preservation of wood, for traces of hydrogen sulphide in water, and many others.

The author is to be congratulated on having produced a book which, owing to its clear arrangement and care in descriptions of practical details, is excellently adapted for rapid laboratory reference, while the theoretical portion and the large number of references to contemporary literature render it valuable to all who are more than routine analysts. JANET W. BROWN.

SULPHURIC ACID AND ITS MANUFACTURE. By H. A. AUDEN, M.Sc., Ph.D. London: Longmans, Green & Co. 1930. Price 16s.

The preface tells us that this book is designed, as the standard works on the subject are so costly and full of detail, "to help the student to grasp the fundamental problems associated with the subject, and by means of the accompanying references to enable him to consult the original articles when more detailed information is required."

It will certainly achieve its second object. The references are most numerous and complete, and, as a classified index to the literature of the subject, the book is

most valuable. Whether it will effectively attain its first object seems open to doubt; and certainly its effectiveness for that object could have been greatly enhanced by more attention to arrangement and style.

The book is divided into sixteen chapters:—1, Historical and Statistical; 2, Properties of Sulphuric Acid; 3, Handling and Transport; 4, Sulphuric Acid from Sulphates; 5, Sulphur and Sulphur Burners; 6, Pyrites Burners; 7, The Chamber Process; 8, Modifications of the Chamber Process; 9, The Gay Lussac Tower; 10, The Glover Tower; 11, Operation of Chambers; 12, Theory of the Chamber Process; 13, Purification of Sulphuric Acid; 14, Concentration of Sulphuric Acid; 15, The Contact Process; 16, Control of Contact Plant.

The descriptions of plant are for the most part very well done, though many of the diagrams are not very helpful, and might well have been omitted; and the accounts of the modifications of the original chamber process that have been proposed, of the working of chambers, and of the views that have been held by various workers both on the theory of the chamber process and on the advantages and disadvantages of different methods of working, are entered into very fully.

The student who has beforehand a general knowledge of the manufacture, and who seeks information on some particular point, will seldom consult the book in vain; but the beginner will find it difficult to acquire from it clear and adequate knowledge of the subject—chiefly because of faulty arrangement, but also through the frequent irrelevant interpolations and the style of the writing, here and there ungrammatical, and frequently involved and far from clear.

Chapter 5, for instance, is headed "Sulphur and Sulphur Burners"; but after some description of the occurrence and extraction of sulphur (in which, by the way, one might have expected some mention of Frasch and his discoveries), we come to spent oxide, zinc blende, and other sources of sulphur dioxide, with descriptions of burners devised to make use of them, after which we revert to sulphur, continuing (and, to some extent, repeating) the subject of nine pages earlier, and only now dealing with sulphur burners. And Chapter 7, "The Chamber Process," begins by discussing nitric acid and sodium nitrate, and the methods of introducing nitrous gases into the chambers, before any mention is made of the chambers themselves—thus it happens, too, that not only are the Gay Lussac and Glover towers mentioned, but influences on their working are discussed, many pages before the towers themselves are described. Many other instances of a similar lack of order could be cited.

On the second count it may be pointed out that in the Chapter on "Sulphuric Acid from Sulphates," several processes are described, the aim of which is the production of sulphates (ammonium sulphate, for example), not of sulphuric acid from them; and at the beginning of Chapter 7 reference is made, with a very elaborate, but not very illuminating diagram, to the manufacture of nitric acid from ammonia, in a place where the *source* of the nitric acid used is a matter of pure irrelevance. Similarly, the description, on p. 69, of Reich's method of determining sulphur dioxide in burner gas is broken into by an interpolation in its

middle of a paragraph on determining oxygen and total acidity; and on p. 149 the two parts of a statement, that 60 per cent. of the loss of nitre is due to one cause and 40 per cent. to others, are separated by another statement that the total loss is 2·68 parts of nitre per 100 of sulphur burnt. These instances are typical, and they make comprehension of the subjects treated much more difficult—for an ignorant learner, sometimes impossible.

With regard to the style, such sentences as "With the exception of greater ease in cleaning the shallow tray type, the Kessler pattern seems to have the advantage of greater output," are all too frequent; and redundancies like, "It melts, *when quite pure and free from water*, at 14·8°," or "By securing an inlet gas *so far freed from impurities as to be* chemically pure," only hinder the reader.

Careless writing is common—"A Study . . . are of interest"; "A knowledge . . . are helpful"; "Between each baffle"; "Much data"; "Dealt with in a four-compartment precipitator, each of which"; and such phrases as "Quite reasonably rapidly," 'Somewhat cold," "Of the order of about," "Rather strictly," 'Rather arbitrary," disfigure the pages frequently. The author is far from being alone, unfortunately, in his use of the misleading, not to say lying, adjective, "water-white" for colourless—but if water is white, what adjective are we to use to describe snow, milk, or chalk?

There are some errors of other kinds which should be noticed. There is surely something wrong in the dates on the fourth and fifth lines of p. 7; as early as 1862, on the Tyne, pyrites had displaced sulphur so far that 73,000 tons of pyrites were burnt, against 2000 tons of sulphur. It is a little difficult to see (p. 13) how Kohlrausch in 1898 could have re-examined and corrected results given by Knietsch in 1901. On p. 16, c is given as the *required* mixture, but we are told how to make one part of a; the formula, for c, should read $x=(b-c)/(b-a)$. On p. 69 the mode of calculation is very badly put, and the formula is wrong: it should read $(11{\cdot}14\times100)/(m+11)$=percentage of sulphur dioxide. On p. 88 it is not the "heat of formation" of chamber acid which is reduced by using water-sprays instead of steam, but the total amount of heat produced in and introduced into the chamber, the argument being that the reduced amount lessens the need for cooling. The phrase (p. 178), "The current, about 620 kilowatts per 24 hours" is perhaps just a slip, but suggests a very hazy idea of the meaning of electrical units.

Some clerical or typographical errors occur; on p. 4, l. 9, *or* should be *and*; p. 42, l. 27, *for* should be *from*; p. 64, l. 23, *same* should be inserted before *low*; p. 67, l. 11, the final *s* of *temperatures* should be deleted; p. 75, the footnote to reference figure 3 is wanting; p. 88, l. 14, *tower* should be *lower*; p. 111, the diagram is lettered "*Glover*" instead of "*Gay Lussac*" tower; p. 126, l. 11, *ton* should be *lb.* (or, perhaps better, "20" in the previous line should be "44800"); p. 213, *channeling* is misspelt.

The book is admirable in its intention, and ought to serve a very useful purpose; and if I have dwelt more upon its defects than its excellences, this is from no desire

to decry it, but from an honest feeling of disappointment that it should fall short of the ideal the author has had in mind, and in the hope that a future edition may be called for, and opportunity afforded for the thorough revision that could enormously improve the book. J. T. DUNN.

A MONOGRAPH OF VISCOMETRY. By GUY BARR, D.Sc. Oxford University Press; London: Humphrey Milford. 1931. Price 30s. net.

Dr. Barr's monograph has supplied a definite need in English literature for a comprehensive collection of methods of viscosity measurement and a critical study of their comparative values. For the most part, the subject of viscometry has been dealt with in rather diverse manners in text-books devoted to wide subjects, such as oil technology. The treatment of the subject in one volume is, therefore, more than welcome.

After a few historical notes Dr. Barr explains the theories of the viscous flow of liquids in tubes, describes the experiments of the pioneers of viscosity measurements, and deals fully with methods for the measurement of viscosity in absolute units. The Redwood, Saybolt and Engler viscometers are discussed under this heading, since their essential dimensions have been chosen so as to give results which can be directly translated in terms of absolute viscosity. This is rather an important finding, since viscometers of this type are often wrongly stigmatised as empirical.

Chapter V deals with capillary viscometers for routine work in which relative values are sufficient and in which liquids of known viscosity are accepted as standards. The precautions necessary in using such viscometers are carefully outlined, and it is emphasised that they can be made to give more accurate results than absolute viscometers in which experimental conditions require more elaborate precautions.

The subsequent chapters deal with viscous flow between parallel plates, capillary tube methods for gases, the falling sphere method and Stokes's law, rotational and oscillational viscometers, and, finally, miscellaneous methods which have been limited in their application, as, for example, the rolling sphere and air bubble methods. The last chapter discusses anomalous systems, such as colloidal suspensions, gels, etc., in which viscosity measurements are affected by other properties. In view of the difficulties of definition of "plastic solids" and "viscous fluids," this chapter might possibly have been amplified.

The book is well written, and the subject-matter is well arranged. Although Dr. Barr states that he has not attempted to give a full bibliography of the literature of viscometry, nevertheless the references given at the end of each chapter form a useful source of such information.

Both author and publishers are to be congratulated upon producing a valuable text-book upon a subject the treatment of which has hitherto been rather diffuse.

J. G. KING.