Aids to the analysis of food and drugs / by T.H. Pearmain and C.G. Moor.

AIDS TO THE ANALYSIS OF FOOD AND DRUGS

PEARMAIN & MOOR

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THE ANALYSIS OF FOOD AND DRUGS.

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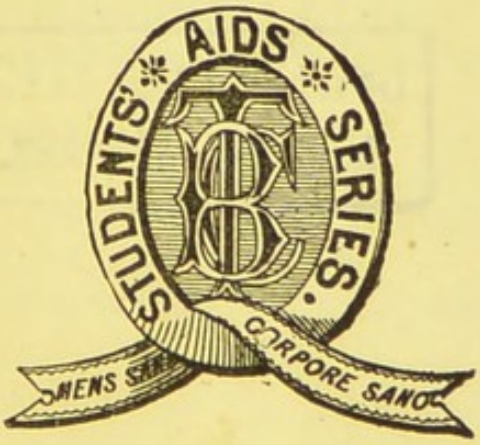

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PREFACE.

As no work of moderate size devoted to the analysis of foods and drugs has recently appeared, we venture to hope that this small book may prove of service to those engaged in the examination of foods and drugs. This work is not intended to be used as a cram-book for examinational purposes. We cannot emphasize too strongly the fact that food analysis is not to be taught in a few weeks, as is frequently attempted in the interest of public health students. A competent knowledge of the analysis of food and drugs is only to be attained by some years of active practical laboratory work.

We have pleasure in acknowledging our indebtedness to the following works :

'The Analyst.'
'Commercial Organic Analysis,' A. H. Allen.
'Foods : Composition and Analysis,' A. W. Blyth.
'Food : Adulteration and its Detection,' J. P. Battershall.
'Analysis and Adulteration of Food,' J. Bell.
'Oils, Fats and Waxes,' J. Lewkowitsch.
'Pharmaceutical Chemistry,' J. Attfield.
'Pharmaceutical Journal.'
'The American Official State Reports.'

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ANALYSIS OF FOOD AND DRUGS.

MILK.

THE composition of cow's milk varies somewhat according to the season of the year, the kind of food employed, and also the breed of cow; but taking the all-round average, it contains about 3·5 per cent. of fat and 9·5 per cent. solids other than fat.

Various causes may produce a milk poorer than this, such as improper food, ill health, old age, and length of time from calving.

These special causes must not, however, be made excuses for the setting up of a too low standard, seeing that it may fairly be argued that milk ought not to be supplied from improperly-fed, unhealthy, or very old cows, nor from a herd who are all allowed to calve together.

The standards adopted by the Somerset House chemists (who are the referees under the Sale of Food and Drugs Act) are 2·75 per cent. of fat and 8·5 per cent. of solids not fat.

This is lower than any other country, except France, the following being some of the standards adopted :

State of New York : water, 88 ; fat, 3.
State of New Jersey : total solids, 12.
State of Massachusetts : total solids, 13.
Paris : total solids, 11·5 ; fat, 2·7.
Berne : total solids, 12·5 ; fat, 3·5.

Dr. Bell, of Somerset House, recently published a table of figures representing the composition of the milk yielded by a number of cows, on which he based the 2·75 standard above mentioned.

These figures have been criticised by abler milk experts than ourselves, and are not generally accepted by analysts as a satisfactory basis on which to formulate a standard.

It is not too much to say that the disgraceful state of the milk-trade in this country is fostered, if not actually caused, by this absurdly low standard, by which, of course, analysts are compelled to abide, or take the risk of being overruled by the referees, who are, naturally, infallible in the eyes of the average magistrate.

Methods of Analysis.

An instrument termed Feser's lactoscope, which depends on the opacity of milk, was used before exact methods of analysis were devised; but both this instrument and the creamometer are too inaccurate to be relied on, or to be used at all, now that we are in possession of methods at once accurate and expeditious.

We will now proceed to describe in detail the methods of analysis ordinarily applied to milk.

Specific Gravity.—Directly the samples are received in the laboratory the gravity should be taken, each sample being carefully shaken first, to mix in any cream that has risen, but avoiding the creation of a quantity of air-bubbles.

Tables may be used to correct the gravity-reading if taken at any temperature to what it would have been at 15·5° C.; but in practice it is easy to bring the samples to the right temperature by standing the bottles in water at 15·5° C.

The specific gravity may be taken either by a delicate hydrometer or (more exactly) by means of a Westphal balance.

The specific gravity of milk is raised by the abstraction of fat, and lowered by the addition of water, hence by partial skimming and watering it may be brought to the same gravity that it possessed before it was tampered with.

Whether, therefore, the specific gravity is normal or not, the fat or the total solids must next be estimated, and in suspicious cases both.

The estimation of the fat is usually performed by some type of centrifugal machine, and afterwards (for confirmation) by either the Adams or the Werner-Schmidt method, descriptions of which will be found further on.

The **Total Solids** are estimated by evaporating 5 or 10 grammes in a shallow platinum dish till constant in weight. Some chemists, to save time, prefer to take 5 or 10 cc. for the determination of total solids after correcting for specific gravity. The time usually allowed for complete drying being three hours *on* and three hours *in* the water-bath, less time is required if platinum dishes are used, and if the bath is kept boiling briskly.

Some operators prefer to work on as little as 2·5 grammes of milk, and add a drop of a mixture of alcohol and acetic acid (which is, of course, evaporated off again) to curdle the milk, thus preventing a skin from forming on the surface, which prevents the escape of moisture.

Dry milk-solids are very hygroscopic, and should be weighed as soon as cold. It is not advisable to leave dishes (particularly platinum ones) varying times in an exsiccator before weighing, as the occlusion of air on their surface causes an increase in weight of over a milligramme in thirty minutes' time.

The **Ash of milk** is usually about 0·7 per cent., but is of little value as an indication of purity, since any deficiency of ash due to added water would often be made up by boric acid or borax, which are to be found in at least one quarter of the samples taken during the summer months.

If we have two out of the three following data, specific gravity, fat, and total solids, we can calculate the third by the use of Richmond's slide-rule. This instrument is generally employed to find the total solids, when we know the specific gravity and the fat ; thus, if we have a milk with a gravity of 1032 and 3·5 per cent. of fat, we shall find on reference to the slide-rule that the total solids are 12·2 ; and if we made a direct estimation, it should vary but little from the calculated figure.

Having obtained the total solids (by calculation), we subtract the fat, and if the solids-not-fat do not fall below the standard, an actual estimation of the total solids is not needed.

The milk-sugar may be estimated by Pavy's* method.

* See sugar in urine.

The **Nitrogen** in milk can be determined by Kjeldahl's method, as in the case of condensed milk.

Estimation of the Fat.—There are several different methods of determining the fat, which may be divided into the following classes :

1. Estimation of the fat by reading off the volume of fat liberated after treatment by chemical means with the employment of centrifugal force. On this principle all the mechanical methods are based.

2. Estimation by simple extraction with a solvent of the milk dried (*a*) without addition (Bell's method) ; (*b*) on blotting-paper (Adams' method) ; (*c*) on chrysotile fibre (Macfarlane's method).

3. Estimation by extraction of the fat by ether from milk, after destruction of the casein by acid (Werner-Schmidt).

Mechanical Methods.—It has long been noticed that if milk is treated with hydrochloric or sulphuric acids and warmed, the fat is freed, and rises more or less completely to the top in globules; if the liquid is whirled in a centrifugal machine, all the fat globules disseminated throughout the liquid will unite to form a clear column.

There are many different forms of apparatus, all of which have their supporters, the one most generally used being that devised by the well-known American chemists, Drs. Leffmann and Beam.

This machine is capable of giving up to 2,000 revolutions per minute, and in skilled hands gives results which agree exactly with the Adams process.

Small flat-bottomed flasks are supplied for use with this machine, holding about 40 cc., and graduated on the neck into eighty divisions, ten of these divisions corresponding to 1 per cent. of fat by weight on 15 cc. of milk.

The procedure is as follows : 15 cc. of milk are run into the bottle, and 3 cc. of a mixture of equal parts of fusel-oil and hydrochloric acid added, the bottle well shaken, and then 9 cc. of sulphuric acid (95 per cent.), which is added slowly with agitation. This fills the bottle to within 3 or 4 cc. of the graduations; the liquid is deep brown or nearly black, and some fat can be seen already separated. Sufficient of a hot mixture of equal parts of sulphuric acid and water is added to bring the

top of the liquid nearly up to the zero mark, and the bottle is then whirled in the machine. If there are not as many samples to be analysed as there are places for, the vacant spaces must be filled by bottles full of water to balance the machine, which would otherwise vibrate.

After two minutes' whirling the machine is stopped, and the bottles examined. If the fat and acid liquid are both quite clear, then the fat column is read off; if the fat or liquid is cloudy, the sample must be whirled again.

There is no need to get the top of the column exactly at the zero mark so long as the fat column is within the graduations. The reading is made from the *extreme top* to the extreme bottom of the fat column.

If there is a cloudy layer between the fat and the acid liquid, it is generally due to careless mixing of the milk and acid. The readings ought to agree within 0·15 per cent. with the Adams figure; if they are much higher the fusel-oil is likely to be in fault, and this may be the cause of serious errors, some samples of fusel-oil having been found to give readings as much as ·4 per cent. in excess of the truth.

The theory respecting the use of fusel-oil is that it assists the collection of the fat globules, but does not itself cause any increase in the fat indicated, as it dissolves in the acid liquid.

This method of fat estimation is most useful on account of its rapidity and, in practised hands, its exactness.

In summer, when milks curdle soon after they are received, it is a great advantage to be able to deal with a considerable number, and to ascertain within a short time which of them are suspicious and will require further work.

(*a*) **Bell's Method.**—This method (used by the referees) is particularly applicable to curdled milks. In such cases the *entire contents* of the sample bottle should be poured out into a large platinum dish and evaporated nearly to dryness. When nearly dry, the milk solids are stirred with a glass rod, so as to bring them into a state of fine division. The solids are finally ground with ether and poured on to a filter, and washed with the solvent till free from fat. The ether having been distilled off, the fat is weighed.

This is without doubt the best way of treating curdled

milks, in which much separation of the curd and serum has often taken place, thus rendering it impossible to work satisfactorily on a part of the sample.

(*b*) **Adams' Method**—5 cc. of the milk are spotted on to an Adams paper, which is allowed to dry and then rolled up. One and a half strips of Adams' paper will absorb 10 cc. of milk, but it is better not to put more than 5 cc. on one paper. After the paper has dried in the air, it is placed in the bath for a few minutes' final drying, and extracted in a Soxhlet. A very handy form of condenser is the hollow metal ball, which is more efficient than a three-foot tube condenser. The fat flask should have a short wide neck, and weigh about 15 grammes; its weight to two places of decimals should be marked on it with a diamond. Sufficient ether (specific gravity 720) should be used to fill the Soxhlet one and a half times, and it should be made to siphon over twelve times at least. It is advisable to place a light screw of paper in the top of the condenser tube to limit as far as possible the entrance of air, which would deposit moisture inside the condenser and wet the ether. Dry ether has no solvent action on milk-sugar, so that nothing but fat will be extracted if the ether is kept dry; but if it contain water, milk-sugar will come out with the fat, and if much moisture gets into the ether it may cause the coil to become damp, and then there may be an error in either direction—*i.e.*, an excess owing to milk-sugar being weighed with the fat, or a loss from fat remaining in the damp coil.

(*c*) **Macfarlane's Method**.—Macfarlane, chief analyst to the Canadian Government, dries 10 cc. of milk on chrysotile fibre, which is packed into a short wide glass funnel. After drying and weighing, a number of these are placed together in a tall glass cylinder and extracted at once with light gasoline. On re-weighing, the loss of weight gives the percentage of fat.

(*d*) The **Werner-Schmidt** method is performed as follows: 15 cc. of milk are placed in a long-stoppered tube, and an equal volume of hydrochloric acid (1·1 specific gravity) added, and the tube heated by being placed in boiling water till its contents are brown or black; it is then cooled, and 15 cc. of ether added, well shaken, and allowed to separate, and the ether blown off by a wash-

bottle fitting. Two similar washings with ether extract the fat completely. The ether solution of the fat is filtered and (if desired) washed with water, distilled to recover the ether, and the fat dried and weighed. It is essential to digest with hydrochloric acid till all the casein is broken up, or the full weight of fat will not be obtained; on the other hand, if the heating is prolonged, too much caramel will be formed, which is soluble in water-saturated ether, and will be noticed in brown drops among the fat.

After considerable experience of both the Werner-Schmidt and Adams methods, we give the preference to the Adams method, as entailing the least time and trouble.

Diseases which may be propagated by Milk.—The most important of these are diphtheria, typhoid fever, and possibly scarlet fever.

Provisions are adopted by the larger dairy companies to exclude from their supply any milk coming from a farm on or near which there is a case of infectious disease.

These regulations are enforced by causing the farmers supplying the milk to sign an agreement whereby they have to notify any case occurring on their farm or in the families of their workmen. Should the farmer fail to do this, he is liable to a penalty. The company also retains the services of the local medical officer of health, who is supplied with forms on which to notify when, in his opinion, it is safe to allow milk from the suspected district to again enter the general supply.

Typhoid fever can hardly be conveyed by milk unless water polluted by typhoid excreta has in some manner entered the milk, having been either deliberately added or used to wash out the pails with.

When cows* are kept in confinement and constantly drained of large quantities of milk, they are liable to become tubercular, and under certain conditions their milk may contain tubercle bacilli. Woodhead, on examining the milk of 600 cows, found 1 per cent. to yield milk in which he was able to demonstrate the bacillus. The death-rate of children from tubercular disease of the intestine is at its highest at about the age when they are chiefly fed on cow's milk.

To demonstrate the Tubercle bacillus in cow's milk,

* Alderney cows are most frequently attacked.

one drop is placed on a cover-glass with two drops of a 1 per cent. solution of carbonate of soda, evaporated to dryness, and stained by the Ziehl-Neelsen method.

The bacillus of typhoid is detected by its surviving the inhibitory action of phenol, whereby the growth of other organisms is prevented. After isolation it is identified by the usual methods.

Pyogenic (pus-forming) organisms may occur in cows from sores on the udder.

In addition to the possible transference of infectious disease from one of the workmen employed on the farm or in delivery, it has been noticed that cows themselves sometimes suffer from a kind of modified diphtheria and scarlet fever, which may produce the ordinary disease in human beings.

In spite of the apparent freedom of sewer air from pathogenic organisms,* there have been several cases of disease in which no other cause could be assigned save that the milk had been exposed to sewer emanations, and hence we cannot afford to neglect this possible cause.

Cow's milk, as ordinarily obtained, contains large numbers of the *Proteus vulgaris*, and those associated with it; when drawn from a healthy cow it is sterile, but in the experience of one of us, milk from apparently healthy subjects sometimes contained the *Staphylococcus pyogenes aureus*.

To render milk sterile, it is sufficient to heat it to nearly boiling for five minutes. But few pathogenic organisms can stand a higher temperature than 60° C., even for a short time.

When epidemics are due to the milk-supply, the following characteristics are to be expected :

1. The outbreak is sudden.
2. Several persons in the same house will be attacked at the same time.
3. A very large proportion of houses attacked will be found to have a common milk-supply.
4. The number of cases per house bear a proportion to the quantity of milk used by them.

The following (non-pathogenic) organisms are sometimes found in milk :

* Law's report to the London County Council. No. 216, December, 1894.

B. prodigiosus
B. lactis erythrogene } producing 'red milk.'
B. indicus

B. syncyanus, producing 'blue milk,' and the *Bacillus Freudenreichii*, producing 'stringy milk'; *Penicellium*, green mould; *Aspergillus*, blue mould; *Mucor*, white mould. The presence of any of these argues dirtiness of the dairy.

Preservatives in Milk.—The following preservatives are frequently found in milk:

(1) Boric acid; (2) Salicylic acid; (3) Formalin. At least one sample in four contains boric acid during the summer months.

There are some nine or ten preservatives sold to dairymen under high-sounding names, which consist of boric acid or borax, or a mixture of salicylic acid and borax.

Salicylic acid is more used abroad than in this country.

Formalin is of recent introduction, and, as so small a quantity (two or three drops to a pint) keeps milk for three or four days, it is likely to be widely used. An addition of ·05 per cent. keeps milk for months.

Boric acid is detected in milk by moistening the ash with alcohol and sulphuric acid and applying a light to the mixture; placed in a dark corner, so little as 1 part of boric acid in 10,000 parts of milk can be detected thus by the green colour communicated to the flame.

The other test for boric acid is to treat the ash with dilute hydrochloric acid, and on introducing a piece of freshly made turmeric-paper it will turn brown, as though it had been moistened with ammonia; the brown colour will change to bluish black when touched with a rod dipped in sodium carbonate.

Boric acid is tested for in butter in the same manner.

Salicylic Acid is not used as much as it used to be, boric acid having largely replaced it. To test for it, first curdle the milk with mercurous nitrate and then shake with ether; evaporate the ether and moisten the residue with ferric chloride, when a blue spot indicates salicylic acid.

Formalin is not easily detected, but if much is present a peculiar sensation is noticed at the back of the throat on tasting the milk, and when hydrochloric acid is added to the milk (as in the Werner-Schmidt method), the casein turns yellow.

As formic aldehyde requires to be added to milk only in

very small quantity, it is evident that its detection, and especially its estimation, presents unusual difficulties. R. T. Thompson has recently made experiments with the object of proving the presence of this substance in milks, and has found that a modification of the well-known reaction with ammonia nitrate of silver gives a good indication of its presence. To apply the test 100 cc. of the milk are carefully distilled until (say) 20 cc. of distillate comes over ; this is transferred to a stoppered tube, and about 5 drops of ammonia silver nitrate added. (This solution is prepared by dissolving 1 grm. of silver nitrate crystals in 30 cc. of distilled water, adding dilute ammonia till the precipitate at first formed is re-dissolved, and then making up to 50 cc. with water.) The mixture of the milk distillate and the silver solution is now allowed to stand for several hours in a dark place (as much as twelve to eighteen hours may be necessary if very little formic aldehyde is present), when, if formic aldehyde is present, a strong black colour or deposit will be produced. A light brown colour should be disregarded ; but, so far as his experience goes, the production of a decided black under these circumstances is only brought out by formic aldehyde, but possibly by other aldehydes also. The usual method of heating with the silver solution in order to obtain a silver mirror is of no value with weak solutions of formic aldehyde. It was found that genuine milks from various sources, when tested by the method described, gave no reaction whatever, even when the distillate was left mixed with the silver solution for twenty-four hours ; or at most gave a slight brown tinge. When as little as 2 grains of the 40 per cent. formalin was added to 1 gallon of milk (which before addition gave no reaction with this process), the distillate from 100 cc. gave a decided black colour, or deposit, intense enough to render the mixture quite opaque. As 2 grains per gallon is a quantity of formalin which would be of little value in the preservation of milk, it is evident that this method of testing is quite delicate enough for the purpose. It ought to be noted that, if a milk contains about 2 grains of formalin per gallon, the 20 cc. distillate from 100 cc. of the milk appears to contain all the formic aldehyde that will distil over, and distillates after that give practically no reaction. A milk containing 7 or 8 grains per gallon

of the preservative may require the distillation to be carried on till 30 or 40 cc. are collected, before it ceases to show a reaction with the silver solution; but in all cases the reaction can be got by distilling over the 20 cc., or indeed 10 cc.*

CONDENSED MILK.

Condensed milk appears to have been first prepared about the year 1856, and is now an article of great importance, more particularly on account of the immense quantity used in the feeding of young children.

We may divide the various brands (in all about fifty) sold in this country into four classes. Many of these brands are the same milk under different names:

1. Unsweetened milks.
2. Sweetened milks.
3. Sweetened partly-skimmed milks.
4. Sweetened skimmed milks.

In most cases the degree of concentration is that obtained by evaporating three volumes to one; that is, the addition of two volumes of water (to an unsweetened milk) will produce a strength equal to the original.

1. The unsweetened milks, of which there are at present three different brands, are all well prepared and keep perfectly. They contain the due proportion of fat.

2. This class forms by far the largest and most important part of the whole supply, and for the most part there is nothing to complain of in them, except that the degrees of dilution recommended would in every case produce a milk below standard. A few of them have been prepared from milk partly deprived of its fat.

3. Many of these, which are stated to be prepared from milk from which a portion of its fat has been removed, are almost entirely devoid of fat, containing less than 10 per cent. of the original fat.

4. Separated milks (sometimes miscalled skimmed milks) are largely used by poor and ignorant people for infant-feeding, and there can be no doubt but that great harm results from this practice.

In some cases the makers honestly state that milk deprived of its fat is unsuitable for the food of infants.

* See also *Analyst*, July, 1895.

The Analysis of Condensed Milk.

The analysis of condensed milk is performed much in the same way as that of ordinary milk, after diluting with water.

The best plan is to weigh 10 grammes into a beaker (having previously well stirred the contents of the tin) and dilute to 100 cc.

We have now a 10 per cent. solution which will serve for the following estimations :

Total Solids.—20 cc. are evaporated in a weighed platinum dish.

Fat.—Two quantities of 5 cc. are placed on Adams papers, dried, and extracted with ether.

Proteids.—10 cc. are evaporated in a Kjeldahl flask and treated as usual.

Milk-Sugar.—10 cc. of the diluted solution are made up to 100 cc. with 40 cc. of water and 50 cc. of strong ammonia.

This 1 per cent. solution is run into 50 cc. of Pavy's* solution, kept boiling.

Total Solids.—The total solids of a condensed milk take at least six hours to dry ; after weighing, the ash may be determined.

Fat.—The Adams process is by far the best for condensed milks. We have made repeated attempts to modify the Leffmann-Beam method, so as to render it applicable to sweetened condensed milks (it works well for unsweetened varieties) ; but the results are usually below the truth, and flocculent matter is often produced which interferes with exact readings.

The Werner-Schmidt method is *not* suitable, and if it is used caramel will be found with the fat, and then it is necessary to dry the contents of the fat-flask to make the caramel stick to the sides.

The flask is then weighed, and the fat washed out with *dry* ether, the caramel remaining in the flask. On re-weighing the difference gives us the true weight of fat.

The method of drying with sand or calcium sulphate, and then extracting with ether, is unsatisfactory, as the fat is extracted with great difficulty.

Milk-Sugar.—The milk diluted as described is run slowly from a burette into 50 cc. of Pavy's solution main-

* For description of process, see 'Urine.'

tained at brisk boiling. In applying Pavy's test to milk-sugar, it must be remembered that the reaction needs more time than is required in the case of glucose.

Using ordinary Pavy's solution and the 1 per cent. solution, it will be found that about 35 cc. of the diluted milk will be equivalent to 50 cc. of Pavy, and the calculation will be as follows :

If 35 cc. dilute milk = 50 cc. Pavy Solution
70 cc. dilute milk = 100 cc. Pavy Solution
or ·7 grams. sample = 100 cc. Pavy Solution
" " = ·05 grams. of glucose

$$\therefore 100 \text{ grams. sample} = \frac{\cdot 05 \times 100}{\cdot 7} \text{ grams. glucose}$$

$$\text{" " } = \frac{\cdot 05 \times 100 \times 100}{\cdot 7 \times 52} \text{ grams. of milk-sugar}$$

It is rarely possible to get the figures representing the separately determined constituents when added up to agree with the total solids in an ordinary milk, but the error is usually small ; hence in the case of sweetened condensed milks it is usual to subtract the sum of the ash, fat, proteids, and milk-sugar from the total solids, and to consider the difference added sugar.

In the case just referred to respecting the difficulty of getting agreements between the sum of the separately determined constituents and the total solids, some of the anomalies observed may be due to the fact that milk-sugar may or may not be dehydrated, according to the manner in which the evaporation has been conducted ; or, again, the proteids may have become altered during the process of condensation, causing them to be incorrectly represented by the ordinary factor.

It appears to be quite time that a definite standard for condensed milk were adopted, say not less than 10·5 per cent. of fat corresponding to a concentration of three volumes to one.

The ratio of proteids to fat is equal in average milk, and if it is found to exceed six to five in condensed milk, it is good evidence that whole milk has not been exclusively employed.

With respect to the statements on the labels, any recommended dilution which would produce a milk below standard, whether whole milk or skimmed milk, should be regarded as fraudulent misrepresentation.

BUTTER.

The amount of butter-fat in butter prepared from cow's milk is about 85 per cent., the remainder being water, casein, or curd, and generally added salt.

Butter varies in colour from white to deep yellow, and is more or less granular in character.

The butter-fat is very complicated in composition, consisting as it does of fatty acids in combination with glycerol, forming triglycerides.

The fatty acids that enter into the composition of butter-fat are : Butyric, caproic, caprylic, capric, myristic, palmitic, stearic, and oleic acids. The first four are soluble in water, and are therefore known as 'soluble fatty acids ;' the latter, being insoluble, are known as 'insoluble fatty acids.'

Dr. J. Bell has published the following analysis of a sample of butter-fat :

	Per cent.
Butyric acid	6·1
Caproic, caprylic, and capric acids ...	2·1
Myristic, palmitic and stearic acids ...	49·4
Oleic acid	36·1
Glycerol (calculated)	12·5

The proportion of butyric acid and its immediate homologues produced by the saponification of butter-fat ranges between 5 and 8 per cent.

The amount of glycerol in butter-fat was first determined by Chevreul, who obtained 11·85 per cent. by direct weighing of the isolated glycerol. Benedict and Zsigmondy, by oxidizing the glycerol with permanganate of potash, and determining the oxalic acid so formed, have found from 10·2 to 11·6 per cent. of glycerol to be formed by the saponification of butter-fat. A. H. Allen has confirmed these experiments.

These analytical results show that butter-fat is essentially a mixture of various triglycerides, those of butyric, palmitic, and oleic acids being the leading constituents :

Tributyrin	Tripalmitin	Triolein.
$C_3H_5(O.C_4H_7O)_3$	$C_3H_5(O.C_{16}H_{31}O)_3$	$C_3H_5(O.C_{18}H_{33}O)_3$.

Some experiments of Dr. J. Bell indicate that the glycerides contain several acid radicles in the same molecule, and therefore the butyrin cannot be separated

by any process of fractional solution from the less soluble glycerides of palmitic and oleic acids. Hence butter-fat probably contains complex glycerides of the following characters:

$$C_3H_5\begin{cases} O.C_4H_7O. \\ O.C_{16}H_{31}O. \\ O.C_{18}H_{33}O. \end{cases}$$

Such a complex glyceride would yield on saponification fatty acids and glycerol in the same proportion as would be obtained from a mixture of butyrin, palmitin, and olein in the ratio of their molecular weights (A. H. Allen, 'Com. Organic Analysis,' vol. ii.).

Margarine.—Margarine, oleo-margarine, butterine, or Dutch butter, as it used to be termed, is prepared by churning melted and clarified animal fats, usually beef or mutton fat, occasionally lard (vegetable oils are now but rarely employed), with skim milk; in this way the curd or casein found in the margarine contracts more or less the flavour of genuine cow's butter. When margarine is carefully prepared and duly coloured, it is not easy to tell the same from pure butter by taste or smell.

Any fictitious butter can now only be legally sold in this country under the term 'margarine,' and must be so marked by a label bearing this name in letters not less than 1½ inches high. If unlabelled, an inspector may require the shopkeeper to supply him with the article as butter, and convictions are often obtained in this manner (see the Margarine Act).

Margarine differs from butter in containing only traces of 'soluble' fatty acids. It consists mainly of the glycerides of oleic, stearic and palmitic acids. The absence of glyceryl butyrate, which is the chief characteristic of butter-fat, is the most valuable means of distinguishing between butter and margarine. On this difference depend the Reichert, Valenta and Hehner tests, the three most trustworthy tests we have for butter.

The Analysis of Butter and the Detection of Foreign Fat.

Water.—Ordinary good butter should contain about 12 per cent. of water; anything over 16 per cent. should be held to be adulteration. Out of 1,500 samples of English

and foreign butter examined by Vieth, Richmond, Bell and others, only 0·6 per cent. contained over 16 per cent. of water ; the larger number contained between 11 and 13 per cent. of water. Where the amount exceeds 16 per cent. it has either been left in by careless manufacture or fraudulently incorporated.

The amount of water can be best estimated by drying 10 grammes in a platinum dish at 105° C. until practically constant in weight ; this will generally be when no crackling noise can be heard when the ear is brought near the dish.

Salt.—The residue, after burning off the fat from the above, can be taken as salt for all practical purposes. The salt in butter may amount to, but does not often exceed, 10 per cent. Dr. Bell found 15 per cent. in one case of English butter.

Casein or **Curd** can be estimated by drying the butter as above, transferring to a filter, and washed with ether until fat-free, and the residue, which consists of casein, weighed. The casein varies from 0·3 to 4 per cent.

Examination of the Fat.—The sample is put into a beaker and placed in the water-bath for a short time, when the water and curd will settle to the bottom. The fat is then decanted and filtered through a dry filter paper. If this is carefully done the fat will be quite clear and bright.

The fat is now examined by the Reichert-Meissl and the Valenta acetic acid test. The indications given by these two tests are generally all that is necessary for all ordinary purposes, but in the case of suspicious or adulterated samples it is desirable to determine the soluble and insoluble fatty acid by the Hehner method, and also to take the specific gravity of the fat.

The **Reichert-Meissl Method** of estimating foreign fat in butter is as follows : 5 grammes of the fat at as low a temperature as it will keep fluid are weighed into a flask, and 2 cc. 50 per cent. NaHO and 30 cc. rectified spirit are then added and the flask attached to a reflux condenser. The flask is then heated over a water-bath, and the contents allowed to boil briskly for twenty minutes. The flask is then detached from the condenser and the alcohol boiled off ; the last traces are removed by gentle blowing with the bellows ; 100 cc. of hot water are then added to the flask and shaken until the soap is entirely

dissolved. 40 cc. dilute sulphuric acid is then run in together with a small piece of pumice-stone to prevent explosive boiling. The flask is quickly attached to an ordinary condenser, and heated with a naked Bunsen flame until 110 cc. have distilled over; the distillation should last thirty minutes. The distillate is mixed and filtered. 100 cc. is then titrated with $\frac{N}{10}$ soda or baryta, using phenol-phthalein as indicator. As 100 cc. was distilled and only 100 cc. titrated, we have to add $\frac{1}{10}$ to the number of cc.'s $\frac{N}{10}$ alkali required.

Leffmann and Beam have published a process wherein glycerine is used instead of alcohol to perform the saponification. This process is much quicker than the alcohol method, with which it gives concordant results. Special flasks with a bulb blown in the neck, which can be placed on the fine balance, can be obtained, which are very much more convenient than using a flask into which the fat has to be weighed by subtraction. Genuine butter-fat requires from 24 cc. to 32 cc. $\frac{N}{10}$ alkali for neutralization.

Margarine-fat and the vegetable oils when tested by this process give distillates, which only require from 0·2 to 1·0 cc. $\frac{N}{10}$ alkali.

From the above data we can calculate approximately the amount of butter-fat in a mixture. Many chemists use half the above quantities; that is, they work on 2·5 grammes of fat, and obtain a distillate of 50 cc., which is titrated direct without filtering. Hence, in speaking of the Reichert figure, it is important to know which procedure has been employed. Of course the amount of alkali required by the distillates in this case is only about half that in which 5 grammes of fat was saponified.

The Valenta Acetic Acid Test.—This test depends on the intermiscibility of butter-fat and strong acetic acid at a low temperature, whereas animal and vegetable fats do not form a clear mixture, except at a much higher temperature. The acetic acid used must be about 99 per cent. This will give a turbidity with genuine butter-fat at from 32° to 36° C. It is best to set the acid against a sample of butter-fat of known purity rather than by titration.

This test is carried out as follows: A test-tube is graduated by running two quantities of 3 cc. of water from a burette or pipette; file scratches are made exactly opposite the dark line forming the meniscus. The tube

is then dried, and 3 cc. each of the fat and acetic acid poured into the tube. The mixture is warmed to 40° C., when, if the sample is butter-fat, the contents of the tube will become clear, whereas margarine will not dissolve in the acid at a lower temperature than 95° C. Mixtures of butter and margarine will of course require intermediate temperatures. In practice we do not note the temperature at which solution takes place, but the point of turbidity (the reverse of solution) begins to appear on removing the source of heat. This is done by stirring the mixture previously heated till clear, with a thermometer, and noting the temperature as soon as the point of turbidity is reached. It makes its first appearance as a tail following the thermometer bulb.*

The Determination of the 'Soluble' and 'Insoluble' Fatty Acids (Hehner's Method). — This method was first devised by Angell and Hehner, but the original process has been modified and improved by Allen, Muter and others.

The following procedure is recommended as the most satisfactory by A. H. Allen, in his 'Commercial Organic Analysis,' vol. ii.

Before commencing the operation, the following standard solutions must be prepared :

(*a*) Dissolve 14 grammes of good stick-potash in 500 cc. of rectified spirit, or methylated spirit which has been redistilled with caustic alkali, and allow the liquid to stand till clear. This solution will be approximately seminormal.

(*b*) A standard hydrochloric or sulphuric acid of approximately seminormal strength.

(*c*) Accurately prepared decinormal caustic soda. Each 1·0 cc. contains ·0040 gramme of NaHO, and neutralizes ·0088 gramme of butyric acid, $C_4H_8O_2$.

A quantity of the butter-fat is melted in a small beaker, a small glass rod introduced, and the whole allowed to cool and then weighed. It is remelted, stirred thoroughly, and about 5 grammes poured into a strong 6 oz. bottle. The exact weight of fat taken is ascertained by reweighing the beaker containing the residual fat.

By means of a fast-delivering pipette, 50 cc. measure

* See a paper on 'The Acetic Acid Test,' by the authors, *Analyst*, July, 1894.

of the alcoholic potash (solution *a*) is run into the bottle, and the pipette drained exactly thirty seconds. At the same time, another quantity of 50 cc. is measured off in an exactly similar manner into an empty flask.

The bottle is fitted with an indiarubber stopper, which is tightly wired down, and is placed in the water-oven, and from time to time removed and agitated, avoiding contact between the liquid and the stopper. In about half an hour the liquid will appear perfectly homogeneous, and when this is the case the saponification is complete and the bottle may be removed. When sufficiently cool the stopper is removed, and the contents of the bottle rinsed with boiling water into a flask of about 250 cc. capacity, which is placed over a steam-bath, together with the flask containing merely alcoholic potash, until the alcohol has evaporated.

Into each of the two flasks is now run about 1 cc. more seminormal acid (solution *b*) than is required to neutralize the potash, and the quantity used accurately noted The flask containing the decomposed butter-fat is nearly filled with boiling water, a cork with a long upright tube fitted to it, and the whole allowed to stand on the water-bath until the separated fatty acids form a clear stratum on the surface of the liquid. When this occurs the flask and contents are allowed to become perfectly cold.

Meanwhile, the blank experiment is completed by carefully titrating the contents of the flask with the decinormal soda, a few drops of an alcoholic solution of phenolphthalein being added to indicate the point of neutrality.

The fatty acids having quite solidified, the resultant cake is detached by gently agitating the flask, so as to allow the liquid to be poured out, but avoiding fracture of the cake. The liquid is passed through a filter to catch any flakes of fatty acid, and is collected in a capacious flask. If any genuine butter be contained in the sample, the filtrate will have a marked odour of butyric acid, especially on warming.

Boiling water is next poured into the flask containing the fatty acids, a cork and long glass tube attached, and the liquid cautiously heated till it begins to boil, when the flask is removed and strongly agitated till the melted fatty acids form a sort of emulsion with the water. When the fatty acids have again separated as an oily layer, the contents of the flask should be thoroughly

cooled, the cake of fatty acids detached, and the liquid filtered as before. This process of alternate washing in the flask by agitation with boiling water, followed by cooling, and filtration of the wash-water, is repeated three times, the washings being added to the first filtrate. It is often difficult or impossible to obtain the wash-water wholly free from acid reaction, but when the operation is judged to be complete the washings may be collected separately and titrated with decinormal soda. If the measure of this solution required for neutralization does not exceed 0·2 cc., further washing of the fatty acids is unnecessary.

The mixed washings and filtrate are next made up to 1,000 cc., or some other definite measure, and an aliquot part carefully titrated with decinormal soda (solution *c*). The volume required is calculated to the whole liquid. The number so obtained represents the measure of decinormal soda neutralized by the soluble fatty acids of the butter-fat taken, *plus* that corresponding to the excess of standard acid used. This last will have been previously ascertained by the blank experiment. The amount of soda employed in this is deducted from the total amount required by the butter-fat quantity, when the difference is the number of cubic centimetres of standard soda corresponding to the **soluble fatty acids.** This volume multiplied by the factor 0·0088 gives the butyric acid in the weight of butter-fat employed.*

The flask containing the cake of **insoluble fatty acids** is thoroughly drained, and then placed on the water-bath to melt the contents, which are poured as completely as possible into the (wet) filter through which the aqueous liquid was previously passed. The fatty acids are then washed on the filter with boiling water, to remove the last traces of sparingly soluble acids. The funnel, with the filter containing the fatty acids, is then placed in a small beaker and put into the water-bath until all the fatty acid that will has run through.

* Thus, suppose an experiment to have given the following figures : Weight of butter-fat taken, 5·120 grammes ; decinormal soda required in the blank experiment, 3·90 cc. ; decinormal soda required to neutralize one-fifth of the solution of the soluble fatty acids, 6·25 cc. Then,

$$\frac{\cdot 0088\ (31\cdot 25 - 3\cdot 9) \times 100}{5\cdot 120} = 4\cdot 70 \text{ per cent.}$$

The flask, funnel, and filter-paper are well washed with ether, and the washings evaporated in a flask to obtain the last traces of fatty acids. The beaker containing the bulk of the insoluble fatty acids, together with the smaller quantity recovered from the ether washings, are dried to constant weight at 100° C. and the two weights added; the sum gives the weight of the insoluble fatty acids contained in the weight of butter-fat taken.

The soluble fatty acids, calculated as butyric acid, should amount to *at least* 5 per cent., any notably smaller proportion being due to adulteration. The insoluble fatty acids from genuine butter-fat rarely exceed 88½ per cent., occasionally reaching 89 per cent., but a sample ought scarcely to be regarded as certainly adulterated unless the insoluble acids exceed 89½ per cent. As a standard for calculation, 88 per cent. of insoluble acids may be regarded as a fair average, the soluble acids being taken at 5½ per cent.

According to J. Bell, the proportion of soluble acids, calculated as butyric acid, not unfrequently falls as low as 4·5, and the percentage of insoluble acids sometimes slightly exceeds 89·0 per cent.

The percentage of adulterant in a butter-fat may be calculated from the following formula, in which F is the percentage of foreign fat, and I that of the insoluble fatty acids:

$$F = (I - 88) \times 13{\cdot}3.$$

Or each 0·1 per cent. of soluble acids above 0·5 may be regarded as showing the presence of 2 per cent. of butter-fat.

The Specific Gravity of Butter-fat.—The method of taking the specific gravity at the ordinary temperature is now but seldom employed, it being more convenient to take the density at temperatures at which the fat is in a molten condition. The temperatures that give the best results, and those that are generally employed, are 37·8° C. (=100° Fahr.) and 99°—100° C.

Dr. James Bell prefers the former temperature. The fat at about 110° Fahr. is poured into an ordinary specific gravity bottle, which is then allowed to stand in water at exactly 100° Fahr. for a few minutes. The stopper is then pushed well home, the bottle wiped dry, cooled and weighed. The weight is then compared with water as 1,000 at the same temperature. As the result of the examination of a great number of samples, pure butter

fat is found to range from 910·7 to 913·5, the greater number falling between 911 and 913. Margarine examined under the same conditions ranges from 901·5 to 906·0.

Allen, Estcourt, and others, take the specific gravity of butter-fat at the temperature of boiling water (98°—100° C.), comparing with water at 15·5° C. as unity.

This is best done with the Sprengel tube. The tube is filled with the melted fat by sucking the contracted end of the tube, the wider end being immersed in the fat. The tube is then placed in water in a state of rapid ebullition, contained in a beaker of such a size that the capillary ends are only just free of the boiling water. When the expansion ceases the tube is set to the mark by the application of filter-paper to the capillary orifice. The tube is then withdrawn, dried, cooled, and weighed. The weight of the Sprengel tube and the weight of the water contained in it at 15·5° C. being known, the weight of fat contained at 99° C. divided by the weight of water at 15·5° C. will give the density of the fat at the temperature of boiling water.

The following are the limits for butter-fat and margarine at a temperature of about 99·5° C. compared with water at 15·5° C. :

Butter-fat	...	...	·8653—·8668
Margarine	...	...	·8560—·8600

The above method may be replaced by the Westphal balance, as recommended by Estcourt. The oil or fat is contained in a wide test-tube, which is immersed in boiling water ; the tube is arranged with a collar, or some other device, to protect the balance from the steam. The plummet is then dipped into the fat, and the specific gravity found as soon as the maximum temperature is reached.

The best form of apparatus with which to carry out this method is that devised by Charles Estcourt, a full account of which will be found in Allen's 'Commercial Organic Analysis,' vol. ii., p. 16. This process leaves nothing to be desired on the score of rapidity and accuracy.

The **Koettstorfer Saponification Equivalent** of butter-fat varies from 242 to 253, the mean figure for margarine being about 284.

The **Iodine Absorption** of butter-fat ranges from 23 to 38 per cent., margarine giving from 40 to 55 per cent. of iodine absorbed. These results, though interesting in

themselves, are not of much value when determining the amount of foreign fat in butter. Further particulars of these two tests will be found under 'Oils and Fats.'

The **Oleorefractometer**, an instrument devised by Messrs. Jean and Amagat, has recently come into use for testing butter and other fats. This instrument is so arranged that a ray of light from a lamp is passed through a chamber containing lard-oil, which is the 'type' or standard oil. In the centre of this chamber is placed a hollow prism, which is filled with the oil or fat under examination. The light in passing through the prism is deflected to a more or less degree, which casts a sharp shadow on a scale, which is placed in the focus of the eye-piece of a telescope attached to the body of the oil-chamber. A collimator is placed in front of the telescope, and the oil-chamber is surrounded by a case to contain warm water, so that observations may be made at any required temperature. The scale is divided into divisions, both right and left of the zero mark. Vegetable oils deflect light to the right and animal oils to the left of the zero. These deflections are noted as + or −; that is, right or left of the zero mark, as the case may be. The liquid oils are examined at 22° C. Butter, margarine, lard, etc., that are not liquefied at this temperature are examined at 45° C.

As the result of the examination of several hundred of samples examined in this instrument, pure butter-fat gives a deflection of from −35° to −23°, margarine deflecting from −18° to −10°.*

On keeping, butter may turn rancid, especially if the butter-milk has not been well washed out; but the changes it undergoes would not under ordinary circumstances be sufficient to very seriously invalidate the Reichert, Valenta or 'Soluble' and 'Insoluble' fatty acid determinations.

It is of interest to mention that one of us found that the fat of the milk yielded by some cows that had been fed on cotton-seed cake gave a decided reduction when tested by the silver test. (See under 'Lard.')

Artificial colouring matters are very frequently added to butter, among which may be mentioned the following:

* For a full description of this instrument, see Lewkowitsch's 'Oils and Fats,' also a paper by one of us, 'On the Testing of Oils by the Oleorefractometer' (*Analyst*, June, 1895).

annatto, turmeric, saffron, saffronette, marigold, and the azo-dyes, the last being of somewhat recent introduction for this purpose. The introduction of artificial colouring into butter is not regarded as an adulteration in this country. It is worth noting that the butter from some Jersey cows often has a very deep yellow colour.

If the colouring matter of a butter can be extracted with alcohol, foreign colouring is undoubtedly present, as the natural colouring matter is not soluble in alcohol.

Butter-fat on exposure to light and air loses its yellow colour, and acquires the smell and colour of tallow.

Preservatives in the form of boric and salicylic acids are sometimes added to butter. We have found boric acid recently in a large number of samples, especially in those coming from abroad.

Boric Acid is detected in the ash, as given under milk.

Salicylic Acid may be estimated by the method as used in the Paris Municipal Laboratory: 20 grammes of the sample is repeatedly exhausted by a solution of bicarbonate of soda, which converts the salicylic acid in the soluble sodium salicylate. The aqueous liquid is acidulated with dilute H_2SO_4, extracted with ether, and a little mercurous nitrate added to the residue after evaporating off the ether, when a precipitate nearly insoluble in water is obtained. This is filtered off, washed, and decomposed by dilute H_2SO_4, free salicylic acid again resulting. It is redissolved in ether, the solvent evaporated off, and the residue warmed from 80° to 100° C. until nearly dry. In order to remove any other acid present, the residue is extracted with neutral petroleum ether, the ethereal solution diluted with an equal volume of 95 per cent. alcohol, and titrated with $\frac{N}{10}$ alkali, using phenol-phthalein as indicator (1 cc. of $\frac{N}{10}$ NaHO = 0·0138 of salicylic acid).

For further identification, the salicylic acid may be liberated again with a corresponding amount of $\frac{N}{10}$ HCl and the liquid tested with a drop of Fe_2Cl_6 solution, when a violet coloration should be obtained.

CHEESE.

This valuable article of food is but little adulterated at the present time, the substitution of foreign fat, that is, of fat other than true milk-fat, as in the case of 'filled' or 'margarine' cheese, being the only one prevalent now.

It is said that starch is occasionally added, but we have never found it in any of the samples we have examined.

There is great need of some definite standard being fixed for cheese, as will be seen from the following table, which shows cheeses varying enormously in the amount of water and of fat that they contain.

Analyses of Various Commercial Cheeses.

	Name of Sample.	Water.	Ash.	Fat.	Reichert cc. $\frac{N}{10}$	Nitrogen.	Casein.
1	Cheddar ...	33·0	4·3	29·5	24·2	4·31	27·4
2	Cheddar ...	35·5	4·2	25·6	28·8	4·39	27·8
3	Cheddar ...	33·8	4·1	30·5	26·4	4·20	26·7
4	Cheddar ...	33·3	3·6	30·6	24·0	4·34	27·6
5	American ...	29·8	3·7	33·9	26·2	4·76	30·3
6	American ...	30·6	3·6	27·7	3·0	4·84	30·8
7	American ...	29·1	3·7	35·3	23·0	4·41	28·1
8	American ...	24·1	3·9	32·0	25·8	—	—
9	American ...	27·0	4·5	30·1	24·8	—	—
10	American ...	25·0	7·9	20·1	30·4	—	—
11	American ...	27·2	4·4	30·9	25·4	—	—
12	American ...	28·1	4·5	33·0	25·6	—	—
13	Gorgonzola ...	40·3	5·3	26·1	22·1	4·36	27·7
14	Gorgonzola ...	33·9	4·6	26·7	23·6	4·06	25·8
15	Dutch	41·8	6·3	10·6	27·0	5·11	32·5
16	Dutch	37·6	6·5	22·5	23·0	4·58	29·1
17	Gruyère ...	28·2	4·7	28·6	30·0	4·93	31·3
18	Gruyère ...	35·7	3·7	31·8	31·1	4·49	28·7
19	Stilton	19·4	2·6	42·2	29·0	4·73	21·1
20	Stilton	21·2	2·9	45·8	32·0	4·14	26·3
21	Cheshire ...	37·8	4·2	31·3	31·6	4·03	25·7
22	Cheshire ...	31·6	4·4	35·3	31·8	4·16	26·5
23	Gloucester ...	33·1	5·0	23·5	31·4	4·99	31·8
24	Gloucester ...	37·4	4·6	28·1	32·3	4·45	28·3
25	Camembert ...	47·9	4·7	41·9	31·0	3·43	21·8
26	Camembert ...	43·4	3·8	22·6	35·0	3·83	24·4
27	Parmesan ...	32·5	6·2	17·1	28·0	6·86	43·6
28	Roquefort ...	29·6	6·7	30·3	36·8	4·45	28·3
29	Double Cream ...	57·6	3·4	39·3	31·2	3·14	19·0
30	Bondon	39·5	0·7	24·4	29·4	1·48	9·4
31	Cream (York) ...	63·1	1·4	6·5	29·0	2·76	17·9

The foregoing table, reprinted from the *Analyst*, July, 1894, shows the results of analyses of a series of cheeses we examined last year.

The following figures call for notice, viz.: Water in the Camemberts, Nos. 25 and 26 containing 48 and 43 per cent. respectively; the York cream, 63 per cent.; the double cream, 57 per cent. Fat is very deficient in the following: York cream, 6·5; Parmesan, 17·1; and the Dutch No. 1, 10·6. The nitrogen is very low in the case of the Bondon cream, namely, 1·48; in the York cream it is 2·6; and in the Parmesan it reaches the highest amount of 6·86 per cent.

Particular attention is called to No. 6 American cheese. This is a margarine cheese, and was bought by the vendor as genuine cheese.

From the above figures we would conclude that none of the cheeses (excepting the Dutch and so-called cream cheese) have been prepared from milk from which fat had been removed.

The following figures, which may be of interest, were obtained by us on some imitations of foreign cheeses which were made in England under the auspices of the British Dairy Farmers' Association:

	Fat.	Water.	Ash.	Nitrogen.	Proteids N×6·3.
Port de Salut ...	36·2	31·3	4·6	4·2	26·5
Caerphilly ...	30·4	24·8	3·4	5·9	37·2
Culommier ...	24·1	37·8	4·1	3·9	24·6
Gorgonzola ...	33·2	33·5	3·5	6·0	37·8
Camembert ...	33·2	35·0	2·9	5·5	34·6
Gervais	69·3	15·8	0·6	3·0	18·9

We found that in flavour they compared favourably with the foreign product.

All cheeses that are not made of milk containing its original fat should be called 'skimmed' or 'separated' milk cheese. At present, on the other hand, we may purchase as 'cream cheese' that which is not even a milk cheese, and if cream cheese is really desired, it must be asked for as 'double cream,' or some other fancy name.

'Margarine' or 'filled' cheese is made by churning separated milk with margarine, curdling and pressing in the ordinary way. If this is sold as cheese, it is a fraud, and the vendor would be liable under the Food and Drugs Act. In the case of foreign cheese sold as English, the Merchandise Marks Act would apply (House of Commons report, *Evening Standard*, March 22, 1895).

In 1885 a special New York State brand was adopted for 'pure cream cheese,' which has had a very good effect, and has accomplished much in the restriction of the sale of the spurious article.

The Analysis of Cheese.

Water is estimated by drying 5 grammes of the samples in thin slices at a temperature of 105° C. till constant in weight.

The **Ash** is estimated on the above by igniting at a low as possible temperature.

Nitrogen is estimated on 1 gramme by the Kjeldahl process (see p. 62). It is essential, however, to use a capacious distillation head, in order to obviate the inconvenience caused by the frothing which often occurs when the sample contains much fat. The proteids are obtained by multiplying the nitrogen figure by the factor 6·3.

Fat.—Many methods may be employed to estimate the fat in cheese. After having given some considerable attention to the matter, we prefer to use one of the two following methods :

Ether Extraction Process.—50 grammes of the cheese is ground up in a mortar with a fairly large quantity of sand. The powder so obtained is placed in a tall stoppered cylinder, and extracted by means of four successive portions of ether, using in all about 500 cc. The ether-washings are then made up to a definite volume and an aliquot portion taken, the ether evaporated, and the residual fat weighed in the usual way.

Mechanical Process.—When it is merely necessary to estimate the fat, it can be quickly and accurately determined by means of the following modification of the Leffmann-Beam process for milk :

2 grammes of the cheese is taken and reduced to as fine a state of division as possible ; it is then transferred

to a small dish and treated on the water-bath with 30 cc. concentrated hydrochloric acid until solution is effected and the solution is of a dark-purplish colour. The mixture is then poured into a Leffmann-Beam bottle and the dish rinsed with the HCl-fusel-oil mixture into the bottle, and, finally, enough of the hot strong acid added to fill the bottle to the mark. It is then centrifugated for one minute.

The Leffmann-Beam bottles are graduated so that ten divisions equal 1·0 per cent. by weight on the 15·55 grammes (=15 cc.) of milk taken.

It follows therefore that the factor, in order to make use of the bottle, will be :

$$\frac{15{\cdot}55}{2}=7{\cdot}77.$$

With very little practice concordant readings are easily obtained, which agree with the ether extraction process already explained.

To obtain fat on which to do further work, it is generally sufficient to chop up about 50 grammes of the sample, which is hung up in a muslin bag in the water-bath ; the fat will generally run out clear. The fat can also be obtained from the remainder of the ether by evaporation in the process already given.

The fat should be examined by means of the Reichert process, as described under butter, to prove that it is true milk-fat. Starch should be tested for by taking a portion of the fat-free residue, boiling with water, filtering, and testing the filtrate for starch, by means of a dilute solution of iodine in potassium iodide. No blue coloration should be obtained.

BREAD.

Bread is made by kneading wheat-flour with water, the coherence of the dough being due to the moistened gluten. The porosity of bread, which is essential to its easy digestion, is produced by enclosing in the dough minute bubbles of carbonic acid gas. This is accomplished in one of three ways :

1. By the use of yeast, which sets up fermentation of a small portion of the starch, forming alcohol and carbonic acid gas.

2. By the use of baking-powders containing an acid salt and a bicarbonate, which on being moistened give off carbonic acid.

3. By kneading the dough with water charged with carbonic acid gas under pressure (Dauglish system).

Bread is very rarely adulterated, and any adulteration in the shape of foreign starches would be difficult to detect, as in the baking the starch-granules are ruptured and lose their shape.

We have also been informed on good authority that it is the practice of many bakers at the present time to use a small quantity of boiled potatoes to their dough.

This addition is said to render the bread white, and does not appear to be made with any fraudulent intent, such as making the bread hold more water, and the quantity of potato added (about 1 per cent.) is not sufficient to effect any economy in flour.

Alum may be detected in bread by the logwood test. The bread should first be soaked in water, the paste thus obtained moistened first with carbonate of ammonia, and then with enough fresh logwood tincture to thoroughly colour the mixture pink.

Flour is treated in the same way after making into a paste with water. If alum is present, a lavender colour appears after an hour or two ; if alum is absent, the pink changes to a dirty pinkish-brown.

Sour bread may give the logwood reaction, and therefore the results must be accepted with caution. If alum is indicated by the logwood test, an estimation of alumina and sulphates will be necessary. It is customary to subtract 16 grains of alum per 4-lb. loaf from the total amount found to allow for the alumina naturally present.

In sampling bread for analysis, a loaf should be divided into three parts as usual, and each portion should be sealed up in a tin after wrapping in oil-paper ; this precaution must be taken, or evaporation will stultify any subsequent work.

When determining the amount of water in bread, it must be remembered that the percentage of water in the crust is about half of that in the crumb, and that care must be taken to work on a duly proportionate mixture

of crust and crumb, to obtain which a large piece should be chopped up finely.

The WATER is estimated by drying till constant at 102° to 103° C., the same quantity being available for the estimation of the ash.

The ASH of all flours and meals is hard to obtain on account of the hard cake of carbon that is formed, unless some special means are adopted.

A good plan is to moisten the carbonaceous mass with strong nitrate of ammonia.

The dish in which the ash is being obtained may with advantage be covered with a strip of platinum.

The most obstinate substances—oatmeal, for example—are speedily reduced to ash by the application of a gentle stream of oxygen, which is conveniently applied by leading it under the lid of the dish by means of a piece of tobacco-pipe stem.

The ash of flour and of bread varies from 0·7 to 1·5 per cent.

WHEAT-FLOUR.

Wheat-flour should not contain more than 20 per cent. of moisture, and should be free from grit and alum. Such adulterations as oat, maize, rice, and potato starches have been found, but they are very rare, on account of their easy detection under the microscope. Wheat-starch has two sizes of granules, one much larger than the other, both being circular.

Flour contains varying amounts of gluten, from about 12 per cent. to 18 per cent.; the gluten is estimated by kneading dough produced from a known quantity of flour with water till all the starch is washed out. The remaining stringy mass is dried and weighed.

In flour from which the husk has been separated there is little or no 'indigestible fibre.'

Jago's doughing test is performed thus: 50 grammes of the sample placed in a dish, and stirred with a rod, water being run in from a burette till a dough of ordinary consistence is obtained.

This may appear to be a somewhat indefinite point, but in practice it is surprising what concordant results can be obtained. The point at which a dough of 'ordinary

consistence' is obtained depends on two things : first, the amount of water present in the flour ; and secondly, the amount of gluten in the sample. The main object of the test is to ascertain the number of loaves which can be prepared from a sack of the flour in question.

Old and damaged flour has been ground up with fresh flour, and the resulting mixture is very liable to go bad.

Such mixtures may be detected by their notable amounts of acid, while good flour is neutral, or nearly so.

BAKING-POWDER.

According to a legal decision,* baking-powder is neither an article of food nor a drug, and consequently may contain alum or anything else. Hence no action can be taken under the Sale of Food and Drugs Act in the case of a baking-powder containing alum ; but if a baker buys and uses this baking-powder he may be convicted, because his bread is an article of food, even if baking-powder is not.

Thus, there is no protection for ignorant persons who may buy such alumed baking-powders for their private use, though the sale of bread prepared with these powders would be illegal.

In nine samples of baking-powder we have recently examined there was no alum. Baking-powders may be tested for alum by mixing with dough and applying the logwood test. Some tartrated powders are said to give the logwood test.

The efficiency of a baking-powder may be estimated roughly by weighing out 1 gramme and placing it in the cup of a nitrometer ; this is corked, and the nitrometer being filled with saturated brine, the tap is opened, and the instrument manipulated so as to wet the baking-powder, which gives off its gas, and after the action is over and the nitrometer levelled, the amount of gas may be roughly ascertained.

We have found 30 to 35 cc. of carbonic acid to be given off by 1 gramme of several of the ordinary powders we have examined.

Baking-powders should not contain large quantities of

* See *Analyst*, xix. 48.

sulphates. They usually consist of a mixture of tartrate of potash and bicarbonate of soda, with some inert material, such as rice-starch.

VINEGAR.

Vinegar has been defined to be 'the product of the alcoholic and acetous fermentation of a vegetable juice or infusion. This definition includes all kinds of brewed vinegar, but excludes wood-vinegar. Brewed vinegar of whatever source will naturally be distinguished from wood-vinegar (acetic acid and water), by containing extractive matters which will remain when the sample is evaporated.

In the case of malt-vinegar, by which we understand vinegar brewed either entirely from malted barley or from a mixture of not less one-third malt and two-thirds barley, we find the extractive matter to range about 2·5 per cent.

The process of vinegar-making is as follows : The malt or malt and barley (the latter finely ground) are 'mashed,' soaked in successive quantities of hot water till all that is soluble is extracted. The clear liquor is then run off into another vessel, and yeast added. Fermentation then takes place, with evolution of carbonic acid. The 'wort,' or 'wash,' is then pumped over piles of birch-twigs placed in high vats, to which a regulated supply of air is supplied. The twigs become coated with *Mycoderma aceti*, 'vinegar plant,' and the alcohol produced by the fermentation is then converted into acetic acid.

Small quantities of other bodies, as acetic ether, aldehyde, etc., are formed, which give malt-vinegar its pleasant taste and smell.

In good working all the alcohol is not converted into vinegar, as a little alcohol improves the flavour and assists the 'keeping' of the finished product, which is generally kept for a year in order that the flavour may fully develop.

Malt-vinegar, whether made from malt or a mixture of malt and barley, yields very characteristic figures on analysis, which distinguish it from glucose vinegar or vinegar brewed from substances other than malt.

Vinegar is sold at different strengths, which are denoted

by numbers as follows: 24 the strongest, and 16 (or diamond corresponding to 14) being the weakest. The intermediate strengths are made by adding water to the strongest. In making the weakest, almost an equal bulk of water is added to the strongest vinegar, and this reduces its sharpness so much that many makers add some distilled vinegar to make it more acid. This may be a convenient method, but it exposes the makers to the danger of their vinegar being accused of consisting partly of acetic acid 'derived from sources other than malt,' as distilled vinegar is undistinguishable from acetic acid.

The lowest-strength vinegar that may be sold contains 3·0 per cent. of acetic acid.

Genuine malt-vinegar varies but very little from the following composition:

Specific gravity at 15·5° C.	=1·019	
Acetic acid	=5·50	per cent.
Extract	=2·50	,,
Phosphorus as P_2O_5	=0·08	,,
Nitrogen	=0·08	,,
Ash	=0·50	,,

If the vinegar in question is one of the lower strengths, of course the other constituents should vary in proportion with the acetic acid.

'Distilled' or 'white' vinegar is largely used in the North of England. It is usually prepared by distilling malt-vinegar; the distillate is generally collected in two receivers: the one nearest the still is the strongest, and is sold as distilled vinegar, while the other is used up as indicated above.

'Wood-vinegar,' so called, is prepared by diluting down acetic acid. This is sometimes coloured with caramel, and sold as malt vinegar. The above is often called in the trade pyroligneous acid; this term, however, properly belongs to the crude wood acid which runs from the condenser when wood is destructively distilled.

Dilute acetic acid is also sold under the name 'white wine vinegar.' In both the above cases the sale is fraudulent.

A small quantity of real 'wine-vinegar' and some 'cider-vinegar' is to be found in commerce, but they are not important enough to warrant description here.

Strong acetic acid, termed 'malt acid,' coloured to imitate malt-vinegar, is sold with directions how to dilute it to prepare a fictitious malt-vinegar.

It is not legal to add any sulphuric acid to vinegar, though this was once permitted under the idea that it was necessary for its preservation. Such addition, however, has been illegal for years. The custom has not quite died out, as several convictions were obtained in the northern counties last year for this offence.

The addition of sulphuric acid causes the total solids to be black instead of brown.

Analysis of Vinegar.

The analysis of vinegar is performed as follows: The **Specific Gravity** is taken with the Westphal balance or specific gravity bottle. If a strong vinegar, *i.e.*, 5 per cent. acetic acid, this should be about 1·019.

Acetic Acid.—10 cc. should be titrated with $\frac{N}{10}$ soda and phenol-phthalein as indicator after well diluting with distilled water, when:

No. of cc. of $\frac{N}{10}$ NaHO × ·006 × 10 = per cent. acetic acid.

The **Total Solids** are determined by evaporating 25 cc. in a tared platinum dish; this, after drying to constant weight, is ignited at a low temperature to obtain the ash. The alkalinity of the ash can be determined, but this figure is not of much value. The phosphates should be estimated by Stock's method (p. 61).

The **Nitrogen** is determined by Kjeldahl's process (see p. 62) by evaporating 25 cc. of the sample in a Kjeldahl flask, by heating over a low flame, and blowing air into the flask by means of a foot-bellows; the evaporation then proceeds very quickly, the process is then carried on in the usual way. If the vinegar is one of the lower numbers (weaker strengths), the figures, as before mentioned, should vary in proportion to the amount of acetic acid present. It is often useful for purposes of comparison to calculate the P_2O_5 and nitrogen as parts per hundred on the total solids, rather than on the original sample, as deviations are then more apparent.

If **Free Sulphuric Acid** is suspected to be present, it

may be estimated by the method as devised by O. Hehner. This process depends on the fact that whenever the ash of vinegar has not an alkaline reaction, free mineral acid has undoubtedly been added.

50 cc. of the sample is evaporated to dryness in a platinum dish with 25 cc. $\frac{N}{10}$ NaHO ; this is then ignited at the lowest possible temperature. 25 cc. $\frac{N}{10}$ HCl is then added to the dish, heated to expel CO_2, then filtered. The filter is washed with hot water, and the washings added to the filtrate. The free acid is then estimated with $\frac{N}{10}$ NaHO and phenol-phthalein. The number of cc.'s of soda used is multiplied by ·0049, which gives the amount of free sulphuric acid in the sample.

TEA.

Tea is now very rarely adulterated, on account of the provision made under the Sale of Food and Drugs Act, whereby tea is examined by the Customs authorities, and any samples found to be adulterated are not allowed to be imported.

Damaged tea used to be destroyed, but is now allowed to be sold for the manufacture of caffeine, after it has been treated with certain chemicals which render it incapable of being sold for human consumption. In September, 1894, a successful prosecution was instituted by the Inland Revenue authorities against some persons in London who had been collecting exhausted tea-leaves from refreshment houses, and drying them to sell for mixing with low-grade teas.

The principal constituents of tea are, caffeine (the active principle), albumen, tannin, dextrine or gum, fibre, mineral matter.

Foreign leaves are practically unknown in this country, but it occasionally happens that samples are met with which contain an undue proportion of stalks and ash. Tea-leaves may be examined by soaking in warm water, and carefully unrolling on a tile ; they can then be compared with genuine leaves. Tea-leaves are covered with minute hairs, which may, however, be partly absent in old leaves. Any addition of exhausted leaves would be detected by the low percentage of caffeine, soluble ash, and alkalinity as K_2O.

The **facing** or **blooming** of green tea with Prussian blue, indigo, etc., to give a bright appearance, used to be common years ago; but the custom has now died out. The Japanese Government, in 1884, made it a criminal offence to adulterate tea. Facing of green tea was, however, justified by the plea that otherwise Japan teas would not suit the tastes of American consumers.

A complete analysis of tea is not often necessary; it is generally sufficient to see that there are no leaves of a suspicious character, and that the total ash, soluble ash, and the alkalinity of the soluble ash, calculated as K_2O, are normal.

Estimation of the Total and Soluble Ash.—5 grammes of the tea, in a capacious platinum dish, is ignited at as low a temperature as possible.

The total ash, after weighing, is washed on a filter, and thoroughly extracted with boiling water until the washings are no longer alkaline. A considerable amount of boiling water is necessary, never less than about 400 cc.

Soluble Ash.—The filter containing the ash insoluble in water is now returned to the platinum dish, and ignited until the filter-paper is completely ashed. The weight of this **insoluble** ash, deducted from the **total** ash, gives the **soluble** ash.

The **Alkalinity** of the **soluble ash** is determined by titrating the washings of the total ash with $\frac{N}{10}$ hydrochloric or sulphuric acid, using methyl orange as indicator. 1 cc. $\frac{N}{10}$ acid = ·0094 K_2O.

Out of 160 samples examined by us, the above constituents varied as under :

	Per cent.		Per cent.
Total ash	4·8	to	7·0
Soluble ash	2·8	„	4·0
Alkalinity as K_2O	1·3	„	2·0

The results are in accordance with those of other observers. C. E. Cribb has recently analysed a sample of 'Lie Tea' (sweepings, tea-dust, etc.), which contained 12 per cent. of ash.

Estimation of Caffeine.—The active principle of tea was formerly known as **Theine**, while the name **Caffeine** was generally given to the active principle of coffee.

They are supposed to be distinct bodies, on account of observed differences in their physiological action; now, however, they are known to be identical, and the name 'caffeine' is applied to both equally.

A. H. Allen, after careful study of all the methods proposed for the estimation of caffeine in tea, found the following method the most convenient:

6 grammes of the finely powdered tea are boiled with 500 cc. of water under a reflux condenser for six hours; the liquid is then filtered through coarse filter-paper, and, together with washings, made up to 600 cc. The liquid is heated to boiling, and 4 grammes of finely powdered acetate of lead added, and the liquid again boiled for ten minutes. The source of heat is then removed, and if the precipitate shows signs of settling rapidly, no further addition of lead acetate is required; and, after giving the liquid a few minutes to settle, it is poured on to a filter, and 500 cc. of filtrate collected. This is then concentrated to 50 cc., and then extracted four or five times with chloroform. On evaporation of the chloroform in a weighed flask, the caffeine is obtained in an almost pure condition.

The amount of caffeine in tea ranges from 1·8 to 3·5 per cent. With the exception of the case of the re-drying of exhausted tea-leaves already mentioned, we cannot find any record of prosecutions for adulterated tea in this country of late years.

T. Macfarlane, the analyst to the Canadian Government, in 1892 examined fifty-eight samples of tea, out of which he found two that had been adulterated with exhausted leaves.

Dr. J. Bell examined a number of exhausted teas, and found them to give the following average figures on analysis:

	Per cent.
Total ash	4·4
Soluble ash	0·7
Alkalinity as K_2O	0·2

It will thus be seen that the addition of exhausted leaves is one of the adulterations most difficult to detect, especially when present in small proportion.

COFFEE.

Adulterations of coffee with any other substance than chicory are almost unknown in this country, though they are still found abroad. We have recently examined a sample of artificial coffee which is sold in France, and has been offered for sale in this country, but has not to our knowledge been met with under the Food and Drugs Act. A description of it will be found further on. In Canada, Macfarlane, on examining 141 samples, found thirty-six adulterated, the adulterants being chicory, and roasted pea, bean, rye, and wheat flours.

In most of his analyses, the fat is about 10·0 per cent. on the pure coffees ; but as fat or oil is added during roasting, this figure may vary. The moisture was about 6·0 per cent., and the gravity, of a 10·0 per cent. decoction, averaged 1009·5 (water 1000).

Coffee-beans have the following average composition :

	Per cent.
Caffeine	1·0
Gummy matter	25·0
Fat	17·0
Tannic acid	20·0
Cellulose	33·0
Mineral matter	4·2

Caffeine in coffee averages about 1·2 per cent. on samples dried at 100° C., and may be determined as in tea. The **moisture**, estimated by drying at 100° C., should not exceed 6·0 per cent. The **ash** is about 5·0 per cent. The most useful qualitative test for chicory in coffee is the behaviour of a pinch of the sample when dropped on to the surface of a glass of water. Coffee remains floating on the top—for some minutes, at least ; while chicory sinks almost instantly, colouring the water in its fall. The fragments which have sunk to the bottom, and are presumably chicory, should be taken out separately, and examined first as to their hardness. Coffee is hard ; chicory is soft. They are then examined under the microscope. The microscopic examination of coffee is best conducted thus : The portion used for the cold water test is boiled, and a drop of the topmost and more

flocculent layer extracted by a pipette. This will be found more characteristic, both in the case of coffee and chicory, than the heavier matter below. Coffee contains a structure of bars not unlike a wooden paling, while chicory (and certain substances with which chicory may be adulterated) shows hollow spiral ducts never seen in coffee.

Starchy matters, such as breadcrumbs, acorns, rye, wheat, bean, pea, or lentil flour, are tested for by applying the iodine test.

Estimation of Chicory.—When chicory is found in coffee, the method employed for its estimation is as follows: 10 grammes of the sample are boiled for some minutes with about 50 cc. of water, set aside for a few minutes to settle, and the clear liquid poured off through a filter, fresh water added to the grounds in the beaker, and the process of boiling and pouring off repeated till the decoction measures nearly 100 cc. It is then cooled, and made up exactly to 100 cc. The specific gravity is then taken by means of a Westphal balance or any other means. **Pure coffee** gives an extract of specific gravity 1009·5 (water being 1000); while **chicory** gives an extract of specific gravity 1025. We may thus consider that every rise of 1·6 in the specific gravity above 1009·5 is equivalent to an addition of 10·0 per cent. of chicory.

Other methods for the estimation of the amount of chicory in a mixture have been used, such as comparing the tints produced by a 10·0 per cent. decoction of the sample with the colour yielded by known mixtures of coffee and chicory; this would hardly be safe to use now, seeing that the chicory may be tainted with caramel.

Another method depended on the fact that, after boiling, coffee still remains hard, while chicory becomes very soft; so that if a known weight of the sample is boiled, poured on to very fine muslin, and rubbed, the chicory may be rubbed through the muslin, while the coffee does not pass through, and may be dried and weighed (W. Blyth).

The sample of fictitious coffee referred to above yields an extract similar to that of pure coffee; but its microscopic appearance would at once distinguish it from genuine coffee, and render its detection certain, even if it were not present in a mixture to a greater extent than

5·0 per cent. It shows indications of the presence of a small quantity of exhausted coffee; but the striking characteristics are the clusters of starch cells, resembling the heads of Indian corn, and the flat network which is totally unlike anything ever seen in coffee; these structures we found to be typical of acorn. On analysis, the sample gave the following figures :*

	Per cent.
Moisture	3·2
Ash	3·4
Soluble	2·7
Insoluble	0·7
Fat	12·3
Caffeine	none
Extract gravity	1009·5

Various 'extracts' of coffee are now sold, and it may therefore be expected that some attempt will be made to work up the grounds, just as was quite recently done in the case of exhausted tea-leaves; so that it may be wise in future to keep a look-out for exhausted coffee in ground coffee. Its presence would probably be revealed by a low extract gravity and low soluble ash.

COCOA.

Cocoa is prepared from the roasted seeds of the *Theobroma cacoa*, which are previously caused to undergo a species of fermentation. It is sold in the form of 'nibs' (partly ground) and in powder. Pure cocoa should contain no addition of starch or sugar, and may with advantage be freed from part or all of its natural fat. Mixtures of cocoa with starch and sugar are allowed by law to be sold as cocoa if the fact that they are mixtures is disclosed on the label; but it would be better to drop the term 'cocoa' and call them chocolate. Some of the leading brands of cocoa are practically free from fat, and their value is certainly enhanced thereby. Some of the cocoas sold as mixtures contain considerably more starch and sugar than they do cocoa.

The addition of starch and sugar is imperative, to enable a dry powder to be produced, unless some of the

* See *Analyst*, xx. 176.

fat is removed, as cocoa naturally contains some 50 per cent. of fat, the greater part of which is removable by hot-pressing. The '*rock-cocoa*' as supplied to the navy contains added starch and sugar. The chief constituents of cocoa are *fat*, *albumen*, *cellulose*, *starch*, *theobromine*, and *mineral salts*.

The fat (*oleum theobromatis*) is used in pharmacy for ointment-making; its estimation is readily effected by extracting with petroleum spirit.

Examination for Adulteration.

It does not seem to be so often adulterated as stated by some authors. Out of sixty-four samples examined by us only four were found to be adulterated.

The **Albumen** in cocoa may be estimated by the use of the 6·3 factor after that due to theobromine has been subtracted; part of this albumen is soluble in water, and is probably its most valuable constituent.

The **Cellulose** is chiefly derived from the husk, which is mostly removed from the better qualities, but is sometimes present in unduly large quantities in the inferior chocolates.

The **Starch** of cocoa, usually about 5·0 per cent., is quite easily distinguished under the microscope from any added sago or arrowroot starches.

Theobromine ($C_7H_8N_4O_2$) contains about 20·0 per cent. of nitrogen, and is the active principle of cocoa, as theine or caffeine is of tea and coffee; it has been found to vary between 0·5 to 1·5 per cent. It may be estimated by extracting 20 grammes of the sample with petroleum-ether. After previously drying at 100° C., the residue is first heated in the water-bath to free it from petroleum-ether, and then extracted with alcohol (specific gravity, ·850), which dissolves sugar, theobromine, tannin, etc.; the alcohol is distilled off and the residue taken up with water and clarified with lead acetate, and the lead afterwards removed by sulphuretted hydrogen; from this liquid the theobromine is extracted by repeated shakings with chloroform. On account of its presence in such variable proportions, it cannot be made of use to determine the amount of true cocoa present in a mixture.

The **Mineral Matters** (ash) of pure cocoa, calculated

on the fat-free sample, are fairly constant, provided no treatment with alkali has taken place. The ash of a pure cocoa is about 5·0 per cent. Blyth found 0·9 per cent. of phosphoric acid in genuine cocoa, and proposed to make this a basis for calculating the amount of true cocoa in a mixture. Other observers have, however, found more phosphoric acid than this, so that this cannot be relied on. Dr. James Bell attaches importance to the cold water extract, but this figure would, in cocoas to which an addition of alkali has been made, be of no value. A complete analysis of cocoa is rarely needed. If the ash is normal and no foreign starch can be seen under the microscope, and the cold water extract does not exceed 18·0 per cent., the sample may be considered satisfactory. If, however, added starch or sugar are found (they are generally present together), it is better to make a direct estimation of them than to trust to any other means of calculating their amount. Ten grammes of the sample are dried at 100° C., placed in a filter-paper cylinder and extracted with petroleum spirit, in a Soxhlet's extractor. The cylinder is then dried, and extracted with specific gravity ·850 alcohol; this dissolves the sugar and a quantity of other matters, which must be removed. This is effected as detailed above : the purified sugar is boiled for ten minutes with 2·0 per cent. hydrochloric acid, neutralized, and the *invert sugar* estimated by the Pavy process.* The residue containing the starch must now be boiled for six hours with 200 cc. of 2·0 per cent. sulphuric acid at the atmospheric pressure, or for one hour at a temperature of 120° C. (15 lb. per square inch) ; this can be conveniently effected by using a screw stoppered bottle placed in an oil bath, or in boiling saturated solution of sodium nitrate. The residue, consisting of *insoluble fibre* and some nitrogenous matter, may be treated with a 2·0 per cent. solution of caustic soda, filtered and washed on the filter with very weak hydrochloric acid, alcohol, and ether, dried and weighed as *insoluble fibre.* It is not improbable that some of the cellulose may not be converted into sugar. In calculating the amount of starch from the sugar obtained by its conversion, it must not be omitted to subtract the amount of starch natural to cocoa, *i.e.*, 5·0 per cent.

* See under 'Urine.'

The following figures were obtained by A. H. Allen on a sample of cocoa nibs and two samples of the leading brands of cocoa essence or soluble cocoa, to which no starch or sugar had been added :

	Cocoa nibs.	Sample A.	Sample B.
Ash	2·53	4·93	8·25
Insoluble in water	1·71	3·50	2·09
Soluble in water	0·82	1·43	6·16
Alkalinity (K_2O) of soluble ash...	0·32	0·49	3·23
Cold water extract	9·72	11·64	18·66
Hot water extract	16·84	20·36	27·16

PEPPER.

Both black and white pepper is obtained from the *Piper nigrum*, the fruit of which is pickled before it is ripe and dried in the sun, which gives the well-known shrivelled appearance. White pepper is produced by soaking the fruit in water to soften the husk, which is then removed by friction. The husk is used to adulterate powdered black pepper, and also used by some makers of sausages and sauces.

The principal constituents of pepper are : Volatile oil, which is present in very small quantity ; acrid resin, which is peculiar to pepper, and gives it the pungency on which its value depends; a neutral principle, piperin, and starch.

The starch peculiar to pepper is readily distinguished from all other starches that might be added by the characteristic microscopic appearance.

A great number of sophistications have been practised in the case of pepper, and as would naturally be expected, analysts have devoted much attention to devising methods for their detection and estimation. After grinding both, black and white peppers are 'graded'—this is performed by bolting through sieves—this tends to cause all mineral impurities to collect in the lower grades. This has been made the excuse for passing adulterated samples as 'genuine, but of low grade.'

The **ash** of *white* pepper should not exceed 2·0 per cent. In the case of *black* pepper the ash should never exceed 8·0 per cent. In either case more than 1·0 per cent. of matter insoluble in hydrochloric acid should be regarded as adulteration. The following is a short abstract of the work that has been done on pepper during the last ten years:

W. Leng, in 1884 (*Analyst*, x. 10), shows that the extracts yielded by true pepper and by mixtures of true pepper with adulterants to ether, alcohol, and water, are of no value in judging of the purity of a sample, and recommends the estimation of the starch.

Heisch (*Analyst*, xi. 86) published a large number of analyses of peppers of known origin, showing that the piperine and starch vary greatly.

Bostock Hill, in 1887, found a pepper adulterated with 24·0 per cent. of clay. About the same time Dr. Bernard Dyer examined some undecorticated peppercorns which had been skilfully faced with some kind of white clayey material to make them simulate white peppercorns.

Campbell Brown, in 1887 (*Analyst*, xii. 23), examined several samples of poivrette, and proved their identity with ground olive-stones. Shortly after this he published analyses of long pepper (*Chavica Roxburgii*), and expressed the opinion that its sale as, or mixture with, true pepper is fraudulent.

A. W. Stokes (*Analyst*, xii. 147), published figures showing how the amount of true pepper in a mixture may be estimated by a determination of the fibre.

F. W. Rimmington in 1888 (*Analyst*, xiii. 81 and 107), published drawings of the microscopic appearance of true pepper and long pepper, showing that the starch of long pepper is larger and more irregular in shape than that of true pepper.

In 1889, Stoddart (*Analyst*, xiv. 37) drew attention to a mixture composed of rice starch, barytes, chalk, and lead chromate, which was being sold to improve the colour of pepper. Shortly after this he discovered steatite in pepper to the extent of 10·0 per cent.

W. Johnstone, in a very complete article in the *Analyst* (xiv. 41), gives results of the examination of thirteen samples of peppers of known origin, and concludes that the estimation of the fibre is of more value

than an estimation of the starch. He finds the fibre to vary from 10·0 per cent. to 15·0 per cent., and would therefore consider that no pepper can be genuine which contains over 20·0 per cent. of fibre. Next to the fibre, he regards the ash as a most valuable indication ; he does not seem to have estimated the phosphoric acid in the ash, which would have been of interest.

We are informed by C. Cassal that in 1892 he met with a pepper containing added woody fibre.

In 1894, E. V. Raumer (*Analyst*, xix. 45) showed the difficulty of detecting the addition of pepper husk to black pepper.

W. F. K. Stock informs us that out of 137 examples examined during the last three years, he found only two adulterated—these contained little chalk. During the five years previous he found several samples containing ground rice and exhausted ginger.

Woody fibre is determined by A. W. Stokes as follows: 1 gramme is boiled for five minutes with 100 cc. distilled water ; 50 cc. of 10 per cent. H_2SO_4 is then added, and the contents of the flask boiled for one hour under a reflux condenser. The contents of the flask are then washed into a double counterpoised filter, well washed with boiling water, then alcohol, and lastly ether. The filter-papers are then dried and weighed. Weight= woody fibre. Mr. Stokes found the following percentages of fibre :

	Per cent.		Per cent.		Per cent.
Black pepper	21·0	to	26·3	average	24·4
White „	12·7	„	13·8	„	13·3
Long „	20·0	„	22·3	„	21·0
Olive stones (Poivrette)	62·2	„	64·2	„	62·5
Rice	0·8	„	1·6	„	1·0

Poivrette is detected by the microscope, which shows the denser ligneous cells, some entire and marked with air spaces, some torn and indistinct. Poivrette is turned reddish in colour by H_2SO_4, and yellow by a solution of aniline acetate.

CAYENNE PEPPER.

Cayenne pepper consists of the ground pods of the *Capsicum annuum*, or the *Capsicum fastigatum*. These

plants are both natives of America, but grow in this country under glass. The latter of these has much smaller pods than the former, and therefore the powder which is produced on grinding them is of a much brighter colour, because the proportion of the one skin which contains most of the colouring matter is greater than in the case of the large podded *Capsicum annuum*.

The difference in colour is so marked that anyone who was not aware that the reason was, as we have stated, the difference of the size of the pods, would think that the brighter one must be tinted with an aniline dye. Various adulterations are mentioned ; in fact, almost anything red is said to have been used. Since the year 1879, when A. H. Allen found 6·0 per cent. of red lead in a sample taken in the neighbourhood of Sheffield, we cannot find any recorded adulterations. It would be a difficult matter to introduce any substance which would not be easily detected microscopically, or in the ash.

The microscopic appearance is that of a cellular structure enclosing occasional drops of oil, but no starch. As in all cases of this description, the sample in question should be compared with one of known origin. The pungency for which cayenne is valued resides entirely in the matter extractable by ether (oil and resin), the residue left after extraction being tasteless. W. Blyth gives the following figures obtained by him on the examination of several samples of genuine cayenne, the mean of his analyses being as follows :

	Per cent.
Aqueous extract of dried cayenne ...	32·1
Alcoholic extract	25·79
Benzole extract	20·00
Ethereal extract	10·43
Ash	5·69
Total nitrogen	2·04

GINGER.

Ginger is the root of the *Zingiber officinale*, a plant that is natural to Asia, but which has been introduced into other countries, the chief kinds now in the market being Jamaica, Cochin, Bengal, African, and Japan gingers. Ginger is ordinarily scraped before it is brought into this

country, and is sometimes whitewashed with carbonate or sulphate of calcium, or treated with bleaching powder or the fumes of burning sulphur with intent to preserve it from the attacks of insects, or to improve its colour. Ground ginger is rarely adulterated with foreign substances, as they would readily be detected either by the microscope or in the ash ; it has, however, been recently adulterated by the admixture of extracted or exhausted ginger from the manufacture of ginger-oil or ginger essence ; the latter is obtained by extracting the ginger with weak spirit. This treatment, of course, removes a considerable part of the essential oil and resin peculiar to ginger. The other constituents are, of course, unaffected. Fluckiger and Hanbury state that from 112 lb. of Jamaica ginger they obtained 4·5 oz. of essential oil, or about 0·25 per cent. This oil possessed the peculiar odour of ginger, but not its pungent taste. Its specific gravity was ·878. A column 50 mm. long deviated the ray of polarized light 21·6°. Dyer and Gilbard (*Analyst*, xviii. 197) by their results on gingers of known origin show that this oil is very variable in genuine ginger. The resin is also apparently very variable. The figure representing the alcohol extract after ether extraction is more constant, and shows a variation of from 2·1 per cent. to 3·8 per cent. in genuine samples, while in exhausted gingers it averaged 1·2 per cent. The ash, both total and soluble, is affected by the extraction with weak spirit ; the average for genuine samples, *i.e.*, 2·7 per cent., being reduced to an average of 0·3 per cent. Further figures on samples of known origin may be seen in a paper by A. H. Allen and one of us (*Analyst*, xix. 124), where it will be seen that the cold-water extract of ginger is of value in determining whether a sample contains exhausted ginger or not, and that this figure, taken in conjunction with an estimation of the soluble ash, gives us the best means of judging of a sample of ginger at present at our command. The cold water extract of genuine ginger is about 12·0 per cent.

It has been suggested by Dr. W. J. Sykes that it might be possible to extract the essential oil of ginger with petroleum ether and leave behind the resinous matters, as proposed by Dragendorff as a general method for the separation of the essential oils from resins.

It is possible that the following method might be of

use in the estimation of the essential oil : 10 grammes of the sample are distilled with water till it is certain that all volatile matter has come over, successive quantities of water being used and the distillates mixed, and then extracted with chloroform, and made up to a known bulk; a portion of this is then treated by the iodine absorption method. (See under Oils.)

A. H. Allen (*Analyst*, xix. 217) found a commercial ginger containing as much as 10·0 per cent. of ash, some of which was sand. On the sample being referred to the Somerset House laboratory it was held that the sample was genuine, but of low quality.

From the above facts it will be clear that we have at present no satisfactory data for judging a sample of ginger, but that if any sample be found to give a soluble ash of less than 1·7 per cent., or a cold-water extract of less than 8·7 per cent., it may be pronounced to be certainly adulterated.

The following figures were obtained by A. H. Allen on some samples of genuine ginger (*Analyst*, xix. 124) :

Analyses of Samples of Ginger of Known Origin.

	Jamaica.	Jamaica.	Jamaica.	Jamaica.	Jamaica.	Cochin.	Cochin.	Cochin.	African.	African.	Average.
Total ash ..	3·90	—	—	3·29	3·45	—	3·81	3·62	3·66	3·90	3·66
Soluble ash ..	3·05	1·41	1·70	1·75	1·71	1·71	2·03	2·04	2·28	2·41	2·01
Cold - water extract ..	14·40	13·25	15·65	12·25	11·85	13·00	8·65	11·65	10·80	10·10	12·12
Moisture ..	13·95	10·98	11·26	12·76	13·96	10·64	13·50	13·25	15·97	13·70	13·0

MUSTARD.

Mustard is the meal produced by crushing the seeds of *Sinapis nigra* and *alba*. It is now but seldom adulterated. Wheaten flour, or starch coloured with turmeric, is the only adulterant frequent now.

As the result of the examination of a large number of

samples of pure mustards, Clifford Richardson found the constituents to vary as under :—

	Per cent.		Per cent.
Water	... 5·0	to	10·0
Total ash ...	... 4·0	„	6·0
Oil (fixed) ...	... 33·0	„	37·0
Oil (volatile) ...	... 0·25	„	1·0
Fibre	... 0·5	„	2·0
Nitrogen ...	... 4·5	„	6·0

Examination for Adulteration.

Microscopical examination will show the presence of foreign starch, etc., as will also the low total ash, which in pure samples never falls below 4 per cent. Added flour or starch is also detected as follows : 2 grammes of the sample is boiled with water, the decoction cooled and filtered ; the filtrate, on testing with a drop of iodine solution, will show the presence of starch.

Turmeric.—This is detected by moistening the sample with ammonia, when, if turmeric is present, an orange-red colour is produced. Turmeric can also be detected as follows : 2 grammes are digested in strong alcohol, filtered, and the filtrate evaporated to dryness. The residue is treated with hydrochloric acid. If turmeric be present, an orange-red colour is produced, which is turned to green and blue by excess of caustic soda.

Fixed Oil.—This being the most constant constituent of mustard, it is estimated to determine the amount of pure mustard in a suspected sample. The oil is extracted with ether in a Soxhlet extractor, or by digesting with warm ether in a flask, filtering and determining the weight of oil left on the evaporation of the ethereal solution. The percentage of mustard is then found as follows :

$$\frac{\text{per cent. of oil} \times 100}{30} = \text{per cent.}$$

of pure mustard. The analytical constants of the fixed oil of mustard will be dealt with under the section on oils.

The volatile oil of mustard (*Oleum sinapis*) is an official preparation of the British Pharmacopœia, which ascribes

to it the following characters : Colourless or pale yellow. Specific gravity, 1·015 to 1·020. Boiling-point about 147·8° C. Dissolves readily in alcohol and ether, and to a slight extent in water. It has an intensely penetrating odour, and a very acrid burning taste. Applied to the skin, it produces almost instant vesication.

Mustard from which the whole or part of the oil has been expressed is sometimes added to the pure article. Such an addition is clearly fraudulent.

Aniline Dyes are stated to be in use in America for colouring mustard which has been adulterated by the addition of wheaten flour.

The New York State Board of Health in 1883 gave legal sanction to the addition of flour or starch to mustard, providing the fact of such addition is marked legibly on the label.

HONEY.

Honey consists of the saccharine substance collected by the bees (*apis mellifica*) from the nectaries of flowers, and deposited by them in the cells of the honeycomb.

The composition of honey is complex, but the essential constituent is a mixture of dextrose and lævulose, and a solution possesses the physical property of turning the plane of polarized light to the left. This property furnishes an easy and accurate method for the detection of the adulterated article, and while we have never met with a pure honey which was not lævo-rotatory, yet there are statements on record which claim that honey has been met with which was dextro-rotatory.

Honey is very largely adulterated ; the substances generally used are glucose and cane-sugar. The former, on account of its low price, is the most common, and, mixed with enough of the genuine article to give it a flavour, is extensively sold as 'pure extracted honey.' One will also find a small piece of genuine comb-honey in a jar, which is filled with glucose syrup. The honey in the comb gradually diffuses itself through the mass, giving the required flavour.

Honey is best examined by means of the polariscope. There are many forms of this instrument in use. Shippen Wallace prefers the Soleil-Scheible type of instrument for

the examination of honey. The 'normal weight' of this instrument is 26·048 grammes—that is to say, 26 048 grammes of pure cane-sugar (sucrose) dissolved with 100 cc. water, and a tube 200 mm. in length filled with the solution will indicate 100 on the scale. *Cane-sugar* and *glucose* will therefore indicate *plus*, and *lævulose*, or *honey*, will mark *minus* the zero. The same weight of glucose will turn the plane so far to the right (or *plus*) that it will exceed 100. The commercial glucose, when the normal weight is used, will indicate from 155 to 170, according to the greater or lesser amount of dextrine present. Pure honey will indicate from – 4 to – 15. Seldom, however, as low as – 15. It will therefore readily be seen that owing to the high dextro-rotatory power of glucose, a comparatively small amount will neutralize the lævo-rotatory power of the honey if added. The same, of course, is true if cane-sugar syrup is added; but in this case the indication will not exceed 100, as will be the case if a sufficient amount of glucose is present.

The mode of procedure is as follows: 26·048 grammes of the honey are taken, dissolved in a flask of 100 cc., and the solution filtered through a small quantity of bone black in order to clarify the solution. A tube of 200 mm. is then filled with the solution and placed in the instrument and the instrument adjusted, the indication of the scale being noted. If *minus*, we may assume that the sample is genuine. If the indication of the scale is *plus*, however, that will indicate that either cane-sugar or glucose has been used; and if the scale indicates more than 100, the presence of glucose is conclusive, but if not we must proceed to learn which. This is accomplished as follows: A solution is prepared as stated, or 50 cc. of the original solution is taken and treated with one-tenth volume of hydrochloric acid, heated at a temperature of 80° C. for a few minutes, cooled and re-polarized. If, now, the scale still reads to the right, the presence of glucose is assured; while if to the left cane-sugar is shown to have been the cause of the original reading being to the right.

The action of the acid is to *invert* the cane-sugar—that is, to change it to a substance which no longer is dextro-, but is lævo-rotatory, and which is termed *invert* sugar, and acts in the same manner as honey. While cane-

sugar can be added to a honey which will not indicate *plus*, yet practically the amount used is so great that such is not likely to be the case.

Temperature has more or less effect on the rotatory power of invert sugar ; consequently all the readings of the solutions should be at a uniform temperature in order for a proper comparison.

The **Water** in genuine honey varies from 15 to 25 per cent., and the ash from 0·1 to 0·9 per cent. O. Hehner (*Analyst*, x. 217) states that the ash of genuine honey is always alkaline, whereas that of artificial glucose is invariably neutral. The addition of commercial glucose may often be detected by the turbidity produced by the addition of ammonium oxalate to a filtered solution of the sample, due to the presence of calcium sulphate, a common impurity in commercial glucose. Artificial comb consisting at least partially of paraffin-wax is now coming extensively into use. *The detection of paraffin-wax* in honeycomb is very easy. Genuine beeswax has a melting-point of about 64° C., whereas paraffin-wax is always lower. Paraffin-wax is not affected by treatment with boiling strong sulphuric acid. Beeswax, on the contrary, undergoes carbonization.

The comb, after dissolving out the honey with water and drying, can be examined by the Koettstorfer process (see under oils). Beeswax requires from 9·2 to 9·7 per cent. of KHO for saponification. Paraffin-wax, on the other hand, is an unsaponifiable body.

LIME AND LEMON JUICE.

Lime and lemon juice contains, in addition to free citric acid, citrates, traces of organic acids other than citric, albuminoid and mucilaginous bodies, sugar, etc. The British Pharmacopœia gives the characters of lemon-juice as follows : A slightly turbid yellowish liquid, with a sharp acid taste ; specific gravity, 1·035 to 1·045 ; citric acid, 36 to 46 grains per fluid ounce (8·3 to 10·7 per cent.). Raw lime-juice contains from 3·5 to 8·0 per cent. of free citric acid.

Lemon-juice is stated to contain, according to R. Warington, from 6·5 to 8·4 per cent. free citric acid.

T. A. Ellwood, who has recently examined a large number of lemon-juices, found the specific gravity to be 1·038 and citric acid 8·6 per cent.; the highest result being 9·8 per cent., the lowest 7·4 per cent. These results tend to show the Pharmacopœial standard to be too high.

The **Free Citric Acid** in lime and lemon juice is estimated by titrating about 20 cc. of the sample with $\frac{N}{2}$ NaHO, using phenol-pthalein as indicator. Each cc. of the semi-normal soda solution used will equal 0·035 of the hydrous citric acid ($H_3C_6H_5O_7H_2O$).

The **Citric and other Combined Acids** are determined as follows: The neutralized juice from above is evaporated to dryness; the residue is ignited at a low as possible temperature. The ignited mass is thoroughly extracted with water, and a known volume of standard H_2SO_4 added; the liquid is then boiled and filtered. The filtrate is then titrated with standard NaHO, using methyl-orange as indicator. The amount of sulphuric acid neutralized by the ash is equivalent to the total organic acid of the sample, as on ignition all the salts of the organic acids were converted into the corresponding carbonates; 49 parts of H_2SO_4 neutralized=40 of NaHO=70 of $H_3C_6H_5O_7H_2O$. The result gives the *total organic acid* in the sample calculated as *citric acid*. By subtracting the free citric acid found from the total will give the *combined acid* as *citric*.

Lime and lemon-juice has been found to be extensively adulterated by the addition of sulphuric and hydrochloric acids. Sulphites, salicylic acid, and alcohol are frequent additions made for preserving purposes.

Free Sulphuric and Hydrochloric Acids may be estimated by Hehner's process as given under 'Vinegar.' Genuine lime and lemon juice contain but small traces of sulphates and chlorides.

Alcohol is estimated by distillation as given under 'Beer.'

Sulphites are best determined by oxidation to sulphates, and determining the sulphates so formed by barium chloride.

Salicylic Acid.—This should be tested for by Fe_2Cl_6. If present the sample is treated with acetate of lead to precipitate albuminous matters, filtered, and the filtrate

to the fact that many of them, the constituents of which cost little, are sold at large profit.

The improvement in processes of manufacture, the advantages of capital and skill, the great increase of knowledge regarding the physiology of nutrition, and the relative food-values of alimentary substances, have contributed to the number and variety of foods for infants and invalids. Whatever constituents have been shown to be of most value, the manufacturers claim their particular preparation to possess. The constituents that are of little value or indigestible are said to be absent, the principles which are easiest of digestion and most valuable to nutrition are asserted to be present.

The materials that enter into the composition of these proprietary foods are very numerous. The most generally used are : (1) various starchy substances, as wheaten, corn, lentil, rice, and maize flours, which may be partly cooked by baking, etc. ; (2) milk-powders and condensed milk, prepared from whole or skim milk ; (3) sugar ; (4) albumin ; (5) malted preparations of starch, milk, etc.

An ideal infant's food should, when mixed with water, produce an emulsion simulating the characteristics and containing the component parts of human milk as far as possible.

For very young children no starchy foods should be used at all. Many children thrive well on sweetened condensed milk diluted with water. The unsweetened brands would probably be better, so diluted as to contain about 3·0 per cent. of fat. There are also milk-powders which possess the proper proportion of needful constituents. The 'humanized' milk preparations which are now largely coming into use have their enthusiastic supporters.

A few of the patent infants' foods contain the right proportion of nutritious material, but by far the larger quantity are composed mainly of starch, which is indigestible in the case of young children, and is the cause of the puffy and bloated appearance often mistaken for robust health.

The composition of infants' foods is so varied and complex in character that it is impossible to give any scheme of analysis that would apply to every case. Almost every preparation requires special treatment for its analysis, but much information will be obtained by ascertaining the following particulars : The amount of water, matter soluble

in cold water, fat, fibre, ash, phosphoric acid, albuminoids, nitrogen.

Moisture is estimated by drying a weighed quantity at 100° C. until constant in weight.

Soluble Matter.—Five grammes is extracted by agitating with 500 cc. cold water, and allowing to stand over-night. The supernatant liquid is then siphoned off and filtered. An aliquot part is then evaporated and dried to constant weight. This residue will give the amount of soluble constituents, such as milk-sugar, maltose cane-sugar, soluble albumin, salts, etc.

The solution can then be precipitated with a slight excess of lead acetate to remove interfering bodies, such as albumin. The excess of lead acetate is removed by sulphuretted hydrogen, and the reducing power of the solution on Pavy's solution estimated. This will give the amount of milk-sugar and maltose. A portion of the solution is then 'inverted' with very dilute hydrochloric acid to convert the cane-sugar into 'invert sugar.' The reducing power of the solution is again estimated by Pavy's method and the increased reducing power calculated to cane-sugar. (See under 'Urine.')

Starch.—Starch, if present, can be estimated by drying the residue insoluble in cold water at a low temperature. About 0·5 gramme of the residue is 'inverted' under pressure, as described under 'Cocoa'; the glucose so formed is estimated by Pavy's method and calculated to starch by dividing the amount of glucose found by the factor 0·9.

Fat.—The fat is estimated by the ether extraction process as given under 'Cheese.'

Fibre.—Wood-fibre is estimated as given under 'Pepper.' Woody fibre should be entirely absent from food preparations intended for infants.

Ash.—The total ash is estimated by igniting 5 grammes in a platinum dish at as low a temperature as possible.

Phosphoric Acid.—Phosphoric acid is estimated by the following modification of the molybdate of ammonia process. The following method was devised by W. F. K. Stock, and after an extended use of it we have found it most accurate. By its use it is possible to obtain exact estimations of the phosphoric acid in foods in a much shorter time than by the old methods.

The ash of the sample is treated with nitric acid, the

solution diluted and filtered. About 20 cc. of strong ammonia is then added, then nitric acid, till the precipitate first formed is quite dissolved. Dilute ammonia is now added till a faint permanent opalescence is formed. The volume of the solution at this stage should not much exceed 70 cc. The solution is warmed to 70° C., and 20 cc. of a 10 per cent. solution of ammonium molybdate run in with constant stirring, which is continued for some minutes. If these directions are carefully carried out, the precipitate is entirely yellow and free from the white molybdic acid. The solution is set aside to cool, when the precipitate is transferred to a small filter, washed with 25 cc. hot water, then with a like quantity of alcohol, and lastly with ether. The filter is placed in the bath to dry. The precipitate is then brushed off the paper into a watch-glass and weighed. The weight thus obtained is multiplied by the factor ·0373, which will give the amount of phosphorus as P_2O_5.

Nitrogen.—This is estimated by Kjeldahl's process. This method, which occupies but a short time, and does not involve the use of complicated apparatus, has almost entirely replaced the combustion process.

It depends on the conversion of the nitrogenous matter into ammonium sulphate, which is subsequently decomposed by an excess of alkali, the liberated ammonia being distilled off and titrated.

From ·5 to 2 grammes of the substance, according to its richness in nitrogen, is weighed out on a watch-glass and brushed into a Kjeldahl flask. To this is added 20 cc. of strong sulphuric acid and 0·7 gramme of red oxide of mercury, and the whole heated for some minutes on a tripod stand.

The flask should be placed in a slanting position, so as to encourage condensation of the sulphuric acid vapours in the neck as far as possible. If the liquid seems likely to become clear, no further addition is needed, but if after ten minutes it is still black, 5 to 10 grammes of potassium sulphate are added and the heating continued. When the liquid has become clear and colourless, or nearly so, the flask is allowed to cool ; 200 cc. water is added, and the whole poured into the funnel of the distilling apparatus. A further quantity of about 200 cc. of water is used to rinse out the flask, which is also poured into the funnel, then 75 cc. of 50 per cent. soda hydrate solution and 20 cc.

of a 4 per cent. solution of potassium sulphide added, the soda to neutralize the sulphuric acid, and the potassium sulphide to prevent the formation of mercur-ammonium compounds. The stop-cock of the funnel is closed and heat applied ; the ammoniacal steam is freed from splashings by its passage through the glass 'anti-splasher.' With this apparatus the most troublesome substances can be dealt with.

The apparatus is constructed as follows : A copper flask, capable of holding 500 cc., is fitted with a rubber cork, through which passes a Soxhlet tube, the other end of which is closed by a rubber cork pierced by two holes ; through one of these passes the stem of a tapped funnel, and through the other the end of a block-tin tube, $\frac{3}{8}$ inch in diameter, which is carried up about 18 inches and then down again, its other end passing through a rubber cork into a tapered glass connector, which dips into 50 cc. of $\frac{N}{10}$ sulphuric acid contained in a 4-oz. flask, which is kept cool by being placed in a vessel of cold water.

The ammoniacal steam condenses largely in the tin tube, and is received in the acid. After about 250 cc. of distillate have been collected, the stop-cock is opened and the burner turned out.

The distillate is cooled by placing the flask under the tap, and then titrated with $\frac{N}{10}$ soda hydrate, till the excess of acid is neutralized, using methyl-orange as indicator.

Each cc. of $\frac{N}{10}$ sulphuric acid neutralized by the ammoniacal distillate corresponds to ·0014 gramme of nitrogen, or ·0017 gramme of ammonia.

Working with ordinary reagents, it will be found that a 'blank' experiment usually requires ·2 cc. of $\frac{N}{10}$ sulphuric acid, hence ·2 cc. should be subtracted from the number of cc. of $\frac{N}{10}$ soda used to neutralize the 50 cc. of acid taken.

Albuminoids are found by multiplying the amount of nitrogen found by the factor 6·33. This will give a very close approximation to the total amount of albuminoids or proteids present, as they contain on the average 15·8 per cent. of nitrogen.

Analyses of some Infants' Foods.

	Milk Food.	Milk Food	Lactated Food.	Cream Emulsion.	Malted Milk.	Raw Flour	Cooked Flour
Water	4·0	5·7	7·7	24·3	2·2	9·5	10·5
Fat	1·9	6·8	1·6	15·3	5·3	0·8	—
Albuminoids ...	11·0	10·5	16·0	8·2	16·9	11·3	10·5
Milk-sugar ...	9·7	5·8	27·0	43·1	50·4	—	—
Malt-sugar ...	—	—	—			—	—
Cane-sugar ...	34·6	36·0	—	—	—	—	—
Starch	33·0	30·8	33·8	—	5·6	71·9	72·3
Ash	1·4	1·2	2·6	2·6	3·1	0·5	0·4
Phosphates (P_2O_5)	—	—	0·3	—	—	—	—

BEER.

Beer is a fermented liquid prepared from malt, flavoured with an infusion of hops. This definition must be extended as follows to embrace beers as brewed at present—a fermented saccharine infusion to which has been added a wholesome bitter. The chief constituents of beer are :

(*a*) Water.

(*b*) Alcohol.

(*c*) Malt extractive, containing maltose, dextrine, albuminoid constituents, salts, etc.

(*d*) Bitter principle.

(*e*) Saline constituents from water, etc.

Strictly speaking, beer should consist wholely of the products of malt and hops ; but malt substitutes, such as malted Indian corn and rice, also glucose, technically known as 'saccharin,' prepared by the inversion of various starchy materials, are now largely used.

It is at present legal to use any saccharine or starchy materials in the brewing of beer, and as the duty is levied on the quantity of soluble saccharine matter made into beer, as estimated by the gravity of the infusion or 'wort,' the exact nature and origin of the fermentable materials employed is disregarded by the Excise authorities. The substitution of bitters other than that of the hop is not an offence under the Food and Drugs Act unless injury to health can be proved by their use.

Beers differ largely in their composition, according to the nature and quantity of material used in their manufacture, and the manner in which the fermentation has been conducted. Two methods of fermentation are in use, the 'High' and 'Low.'

The 'high' or surface fermentation is used in England. It takes place at a higher temperature, and is of shorter duration than the 'low' or 'sedimentary' process.

The 'low' or 'bottom' fermentation is largely employed in Germany. The yeast is a different variety to that used in English breweries. The beer is fermented at a low temperature, the yeast remaining at the bottom of the vat. Beers prepared by this process are highly charged with gas, and contain a much larger quantity of extractive matter and less alcohol than those prepared by the 'high' or English process. These beers are very liable to undergo a secondary fermentation unless kept at a very low temperature.

The best-known varieties of malt liquors are :

1. Pale and bitter ales, made from the finest pale malt, and bitter derived from hops in excess.
2. Mild ales, rather sweet, and containing less bitter and more alcohol than the pale ales.
3. Porter, a rather weak liquor coloured and flavoured with roasted malt, which gives it its black colour.
4. Stout, a stronger variety of porter.
5. Lager or German beers, prepared by the 'low' fermentation process, and, as before stated, containing more extractive and less alcohol than English brewed beers.

Analysis of Beer.

Alcohol.—Alcohol is estimated by direct distillation, or by the indirect method.

Direct Distillation.—About 100 cc. of the sample is rendered just alkaline with caustic soda, a little tannin added (to prevent frothing), and the liquid distilled until about 90 cc. of distillate have collected. A small piece of pumice-stone or platinum-wire placed in the distillation flask will prevent bumping. The distillate is cooled to 15·5° C., made up to the 100 cc. mark with distilled water, mixed, and the specific gravity taken with a bottle or

Westphal balance. The amount of alcohol is then found by means of the alcohol tables.

Indirect Method.—This process was devised by Tabarie The specific gravity of the original liquid is first accurately determined. A measured quantity, say 100 cc., is then boiled until all the alcohol and other volatile matters are evaporated off. This will generally be the case if the liquid is boiled down to one-third of its original bulk. The residue is then cooled and made up to its original bulk with water, and the specific gravity taken at 15·5° C., when

$$\frac{\text{Sp. gr. of the original liquid}}{\text{Sp. gr. of the 'extract'}} = \text{Sp. gr. of alcohol evaporated.}$$

The percentage of alcohol is found by reference to the alcohol tables.

The Extract.—5 cc. of the sample is evaporated in a flat-bottomed platinum dish, and dried at 100° C. until constant in weight. The extract may also be estimated with fair accuracy from the de-alcoholized liquid obtained by Tabarie's method of determining the alcohol. The specific gravity of the 'extract' at 15·5° C. is taken, and the excess above 1,000 divided by 3·86, when the dividend is the number of grammes of dry 'extract' contained in 100 cc. of the sample.

Ash.—The ash is obtained by igniting the extract at a low temperature.

Sodium Chloride.—Common salt is determined by exhausting the ash with water, and estimating the chlorides with $\frac{N}{10}$ $AgNO_3$, using neutral potassium chromate as indicator. Each cc. of $\frac{N}{10}$ $AgNO_3$ = ·00585 NaCl or ·00355 chlorine. Salt is now but rarely added to beer in excessive amount. It is often stated that 50 grains per gallon is permitted by the Inland Revenue. This is an error, the origin of which was that the Board of Inland Revenue instructed their officers that in cases in which the chlorides in beer did not exceed 50 grains per gallon as sodium chloride, it was unnecessary to inquire into the origin of the same.

Acidity.—The acidity of beer is partly 'fixed' and partly 'volatile.' The former consists principally of lactic acid, with a little succinic acid. The volatile acid consists mainly of acetic, with traces of other acids.

Fixed Acid.—About 20 cc. of the beer is diluted to 100 cc., and evaporated down to about 50 cc. This is

again diluted, titrated with $\frac{N}{10}$ sodium hydrate, using litmus as indicator. The number of cc. of $\frac{N}{10}$ NaHO used multiplied by ·009 = fixed acid as lactic.

Volatile Acid.—20 cc. of the original sample is well diluted with water, and titrated with $\frac{N}{10}$ NaHO, using litmus as before. The number of cc. of alkali used are then noted. From this is deducted the number of cc. of NaHO required for the fixed acid. The remainder multiplied by ·006 will give the amount of volatile acid as acetic.

Determination of the Bitter Substance.—The bitter principles used to flavour beer are derived from hops, quassia, gentian, calumba, chiretta, etc. These bitters are mostly of the nature of glucosides. Noxious bitters, such as those of *Cocculus indicus* (picrotoxine), nux vomica (strychnine), and picric acid, have been stated to have been used in the past, but their occurrence now is exceedingly unlikely.

1,000 cc. of the sample is concentrated by evaporation to one-half and precipitated boiling with neutral lead acetate ; the liquid is boiled for fifteen minutes, and filtered hot. The filtrate is treated with a slight excess of sulphuric acid. The lead sulphate is filtered off, and the clear acid filtrate gently evaporated to about 100 cc. The excess of acid is removed with chalk, and the liquid filtered. The filtrate is then tasted. If it is free from bitterness, hops have been used to bitter the beer. On the contrary, if the residue is bitter, quassia or some other hop substitute has been used.

The liquid is acidified with dilute sulphuric acid and well extracted with chloroform, which is separated and evaporated. The residue, if bitter, may be due to *gentian*, *quassia*, or *calumba*.

The aqueous liquid, after extraction with chloroform, is shaken with ether. The ether will extract the bitter of *gentian*, *calumba*, and *chiretta*.

The extract left on the evaporation of the ether is dissolved in a little alcohol, hot water added, and the hot solution treated with ammoniacal lead acetate. The liquid is filtered, and the residue and filtrate treated as follows :

(*a*) The precipitate is heated with water, and decomposed with sulphuretted hydrogen. The filtered liquid is bitter in the case of *gentian*.

(*b*) The filtrate is heated with an excess of dilute sul-

phuric acid, filtered, and tasted. Bitter taste indicates presence of *calumba* or *chiretta*.

The aqueous liquid, if still bitter after extraction with chloroform and ether, is rendered alkaline with ammonia, and shaken with ether-chloroform. A bitter extract may be due to *berberine* (*calumba*) or *strychnine*. Portions of this extract may be tested as follows :

On treatment with concentrated sulphuric acid, the residue will turn olive-green in the case of *berberine*, whereas no effect is produced if *strychnine* be present.

(*a*) A portion of the residue is dissolved in HCl, on the addition of chlorine-water ; a red colour will be produced if *berberine* is present.

(*b*) On the addition of concentrated sulphuric acid, together with a trace of powdered potassium bichromate, the residue will turn blue, passing quickly to violet, and red if *strychnine* be present.

Preservatives.—Preservatives are frequently added to beer in the form of salicylic and boric acids.

Salicylic Acid may be detected as follows : About 200 cc. of the beer is concentrated by evaporation to 50 cc. at a gentle heat, cooling and extracting with ether. The ethereal solution is evaporated, and the residue dissolved in warm water. On the addition of Fe_2Cl_6, a violet coloration will be produced if *salicylic acid* be present.

Boric Acid can be tested for in the ash of the beer as described under 'Milk.' A beer 'preservative,' in somewhat extensive use, is a mixture of boric and salicylic acids prepared by dissolving salicylic acid in a solution of boric acid and borax.

Saccharine (*Benzoyl Sulphonic-imide*).—The use of this sweetening agent has been prohibited by the Commissioners of the Customs and Inland Revenue (May, 1888).

For the detection of saccharine in beer and wine, C. Schmitt recommends that 100 cc. should be acidulated with sulphuric acid, and shaken with 50 cc. of a mixture of equal measures of ether and petroleum spirit. After separating the upper layer, and agitating the aqueous liquid with another quantity of the ethereal mixture, the ether-petroleum is evaporated with a little caustic-soda solution, the residue is then carefully heated to 250° C. for a short time ; the residue is then taken up in water, and the solution tested for salicylic acid. If this is found, saccharine was present in the liquid. Of course the

absence of salicylic acid in the original liquid must be first ascertained.

Determination of the Original Gravity of the Beer Wort.—The 'original gravity' of the wort is sometimes required, as a 'rebate' or 'drawback' is allowed when beer is exported. The duty on beer is calculated from the strength of the 'wort' as indicated by its specific gravity. By the process of fermentation the specific gravity of the wort is diminished to an extent dependent upon the amount of alcohol formed. The weight of alcohol being approximately half of the saccharine matters destroyed by the fermentation, it is evident that a determination of the alcohol in the fermented liquid would give the means of ascertaining the quantity of sugar destroyed, and hence of making the necessary correction for the reduction in the density of the wort caused by the fermentation.

The alcohol is first carefully estimated by the direct distillation process. The specific gravity of the distillate is deducted from 1000, the difference is the *spirit indication*. Now find from the following table the number of degrees of 'gravity lost'; thus, suppose the spirit indication is 11·5, take 11 in the first column, and under ·5 in the seventh column we find 51·7 equal to 'gravity lost.'

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	—	·3	·6	·9	1·2	1·5	1·8	2·1	2·4	2 7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·4	75·3	75·9

This figure is added to the specific gravity of the de-alcoholized beer obtained as described under Tabarie's method of determining alcohol. The result is the 'original gravity' of the wort.

Example—

	1000·0
Specific gravity of alcoholic distillate	993·6
Spirit indication=	6·4
= Gravity lost (see table)	26·0
Specific gravity of de-alcoholized beer	1014·2
Original gravity of wort=	1040·2

Analyses of some Typical Beers by Various Authorities.

	Sp. Gr. at 15·5° C.	Alcohol (% by Weight).	Extract.	Ash.	Acidity as Acetic.	Albu-minoids.
Bitter Ale	—	5·4	5·4	—	0·1	0·16
Burton Mild ...	—	5·4	5·1	—	0·1	0·21
Burton Mild ...	—	6·8	6·7	—	0·2	0·26
Burton Pale ...	1·0106	5·3	5·1	—	0·2	—
Scotch Pale... ...	—	8·5	10·9	0·3	0·2	0·74
Bass's Pale	1·0138	6·2	7·0	—	—	—
Alsopp's Pale ...	1·0144	6·4	4·4	—	0·3	—
Stout, Guinness X.	—	6·6	7·2	—	0·2	—
Stout, Guinness XX.	1·0244	5·0	5·5	—	0·2	—
Porter	1·0207	5·4	6·0	—	—	—
Porter, Barclay ...	—	5·4	6·0	0·4	0·2	—
Lager, Pilsen ...	1·0130	3·5	5·1	0·2	—	—
Lager, American ...	1·0162	2·8	6·0	0·3	0·3	0·45
Lager, Munich ...	1·0110	5·1	5·0	0·2	—	0·83

WINE.

Wine is the fermented juice of the grape. In the preparation of wine the grapes are generally separated from the stalks, and then placed in a press and the juice expressed. The juice or 'must' is then placed in vats, in which the fermentation takes place spontaneously. The addition of yeast is unnecessary, as the requisite amount exists naturally on the skins of the grape. The juice before fermentation contains about 20 per cent. of solid matter, of which from 12 to 18 per cent. consists of glucose, the remainder containing albuminous matters, potassium-hydrogen tartarate, calcium tartarate, traces of gum, colouring matter, mineral matter, etc. During the fermentation the glucose is converted into alcohol and carbon dioxide. After the fermentation has ceased, the wine is separated from the 'lees' or residue, which consists largely of yeast-cells and potassium-hydrogen tartarate, and run off into casks, in which an after-fermentation takes place, resulting in a further deposit of tartarates, etc. The wine is then drawn off into fresh casks, in which it is kept for various periods to 'age' or 'mature.'

Wines may be divided into various classes as follows, according to the country of their production: French—clarets, burgundy, champagne; German—Rhine, Moselle; Spanish—port, sherry, madeira; Italian, Hungarian, Greek, Cape, Californian, and Australian, etc.

Wines may be classed broadly into red and white, also by their general characteristics 'dry' and 'sweet.' The 'dry' wines, such as Burgundy, Rhine, Moselle, and Gironde, etc., contain no sugar and a comparatively large amount of acid. The 'sweet' wines, as port and madeira, contain a considerable amount of undecomposed sugar.

The nature of wine is largely influenced by the place of growth, climate, temperature, in addition to the amount of glucose and acids contained in the original grape-juice.

The proportion of sugar and acid best adapted for the production of wine is 40 to 1. If these conditions do not obtain in the natural juice, additions are made so as to satisfy these requirements. If the acid is in excess, the 'must' is diluted and the necessary amount of sugar added

in the form of glucose or cane-sugar. This process is largely used in the champagne country.

The sweet wines are frequently 'fortified' by the addition of alcohol, generally in the form of brandy ; this is to prevent the unfermented sugar from undergoing subsequent fermentation. The proportion of alcohol in 'fortified' wines is sometimes as high as 22 per cent., but in natural wines it never exceeds 13 per cent.

By the English Customs regulations 10 per cent. of brandy is allowed to be added to wines in bond, while in France the sophistication is permitted in wines intended for export, provided the total amount of alcohol does not exceed 21 per cent.

The total solid matter of wines ranges from 1·8 to 3·4 per cent. ; the mineral matter from 0·35 to 0·15 ; the acidity, as tartaric acid, from 1·0 to 0·5 ; glycerine from 1·3 to 0·6 ; phosphoric acid from 0·06 to 0·02 per cent.

The 'plastering' of wines consists in adding calcium sulphate (plaster of Paris) to the 'must' or the wine. This addition is claimed to add to the keeping properties of the wine by removing any excessive acidity. This addition is very detrimental, as it gives rise to the formation of free sulphuric acid and acid sulphates, as well as calcium tartarate and potassium sulphate. The calcium salt, being insoluble, is deposited with the 'lees' ; the potassium sulphate remains in solution, and as it exerts a decidedly purgative action on the body, its presence cannot fail to be detrimental. In France, the sale of wine containing over 0·2 per cent. of potassium sulphate is prohibited. The plastering of wines is chiefly carried on in Spain, Portugal, and the South of France. The ash of pure wine does not exceed 0·35 per cent., but in samples of sherry often met with it reaches 0·5 per cent., and is composed almost entirely of sulphates.

Many of the Continental wines are mixed or blended, especially for export purposes ; this probably constitutes the most frequent form of adulteration. Natural wines of the same manufacture vary to some extent from year to year in colour, flavour, and other characteristic properties, so mixing is resorted to in order to supply the trade with a product always possessing the same qualities. In many cases, the flavour of the wine is improved by blending, and also the intoxicating effect increased, both results being due to some extent to the compound ethers formed.

From the chemical point of view, the most important constituents of wine are the primary constituents of the fermentation, such as the alcohol, glycerine, acids, etc.; but the commercial value is far more dependent on the flavour and bouquet, which are due to the compound ethers, or 'esters,' of acetic, caproic, caprylic, tartaric, and other organic acids. The total amount of ethers is very small, 0·3 per cent. at the maximum. 'Pasteuration,' as largely used in France, is a process to effect the artificial ageing, and to promote the keeping qualities of the wine. This is accomplished by subjecting the bottles of wine to a temperature of from 50° to 100° C. for several hours. Wines which exhibit ropiness and other diseases are restored by this treatment, which causes the destruction of the disease organisms.

Pure cultures of the various micro-organisms procured from the high-class vintages are now largely coming into use to improve the lower grade wines, and also to give to fictitious wines some of the flavour and bouquet of the genuine article.

It is stated that over 100,000,000 gallons of fictitious wine was manufactured in France during last year (1894). The greater part of this is made from dried raisins imported from Spain and the Levant. F. Schaffer (*Zeits. Anal. Chem.*, xxiv., p. 559) has published the following analysis of these artificial wines:

	A. Per cent.	B. Per cent.	C. Per cent.
Alcohol	8·05	9·55	7·02
Extract	2·39	1·96	1·80
Sugar	0·33	0·41	0·32
Ash	0·21	0·13	0·16
Acidity (as tartaric) ...	0·74	0·50	0·77
Cream of tartar ...	0·26	0·23	0·47
Phosphates (as P_2O_5) ...	0·02	0·01	0·02

So-called 'unfermented wines' are now extensively sold in the temperance interest and for sacramental purposes. They generally consist of clarified fruit juices preserved with salicylic and boric acids, often with the addition of saccharine.

The Analysis of Wines.

Specific Gravity.—This is taken at 15·5° with a bottle or the Westphal balance.

Alcohol.—Alcohol is estimated by direct distillation as given under 'Beer.' It is better to take 50 cc. and dilute to 100 cc. with water, and multiplying the indicated amount of alcohol as given by the tables by 2 to obtain the percentage of alcohol. The direct method of Tabarie can also be used. (See under 'Beer.')

Extract.—This is estimated by drying 5 grammes as described under 'Beer.' A very close approximation can be obtained as follows: From the specific gravity of the de-alcoholized liquid is subtracted 1000; the remainder divided by 4·6 will give the number of grammes of extract per 100 cc. Another method of calculating the total solids, which is preferable in the case of very sweet wines, is to divide the difference between the specific gravity and 1000 by 3·86 instead of 4·6, and subtract the percentage of ash from the figure so obtained. This method is based on the assumption that the organic solids of wine have the same solution density as extract of malt, and that the mineral matters have twice that density.

Sugar.—The sugar of natural wine consists wholly of glucose. It is estimated by boiling off the alcohol and removing the colouring and other reducing bodies by a slight excess of basic lead acetate, filtering, removing the excess of lead by suitable means, and the reducing power of the liquid on Pavy's solution estimated. 100 cc. of light wines, or 50 cc. of sweet wine, treated as above and diluted to 200 cc., will give solutions of suitable strength for the above test.

Ash.—The ash is obtained by igniting the dried residue at a low temperature.

Phosphoric Acid.—This is estimated on the ash by Stock's process as described under 'Infants' Foods.'

Acidity.—The acidity of wine exists both as fixed and volatile. The former consists principally of tartaric, the latter of acetic acid.

Fixed Acid.—This is determined by diluting 20 cc. of the sample with water, boiling down to a low bulk, again diluting, and boiling down as before. The residue is taken up in water, and titrated with $\frac{N}{10}$ NaHO, using phenol-

phthalein as indicator. The number of cc. of soda used multiplied by ·0075=*fixed acid as tartaric.*

Volatile Acid.—20 cc. of the original wine is well diluted with water, and titrated with $\frac{N}{10}$ NaHO, using phenol-phthalein as before. The number of cc. of alkali used in the case of the fixed acid is deducted from the result. The remainder multiplied by ·006=*volatile acid as acetic.*

Free Tartaric Acid and Potassium Bitartrate.—In the presence of a small amount of free acids, the detection of a considerable amount of free tartaric acid may fairly be considered as strong evidence that the wine is artificial. Nessler recommends the following qualitative test : 20 cc. of the sample is repeatedly shaken with a little freshly and finely ground cream of tartar. After standing one hour, the solution is filtered, 3 or 4 drops of a 20 per cent. solution of potassium acetate is added, and the mixture is allowed to remain at rest for twelve hours, when, in presence of free tartaric acid, a precipitation will take place. The quantitative estimation of free tartaric acid and potassium bitartrate is made by Berthelot's method as follows : Separate portions of the wine (20 cc. each) are introduced into two flasks, a few drops of 20 per cent. solution of potassium acetate being added to the second flask. 200 cc. of a mixture of equal parts of alcohol and ether are then added to both flasks ; their contents are repeatedly shaken, and finally set aside for eighteen hours at a temperature between 0° to 10° C. The separated precipitates are now washed with the ether-alcohol mixture, and then titrated with $\frac{N}{10}$ NaHO solution. That formed in the first flask corresponds to the *potassium bitartrate* originally contained in the wine. The second represents the *total tartaric acid* present. The addition of a small quantity of clean sand will assist in the separation of the precipitates.

Detection of Foreign Colouring Matter.—Many processes and tests have been published from time to time to detect foreign colouring in wine, but very few of them are of any practical use. A very simple method has been devised by Dr. Dupré to determine the presence or otherwise of foreign colouring in wine. A 10 per cent. solution of the best transparent gelatine is prepared, which is then run into a mould to set. The hard jelly is then cut up into

small cubes about $\frac{3}{4}$ inch square. Two or three of these are placed in the suspected sample of wine. After standing in the wine for twenty-four hours the cubes are removed, washed with a little cold water, then cut in half. On examining the section, in the case of genuine wines, the colouring matter will not have penetrated more than about $\frac{1}{16}$ inch. The majority of the foreign colourings added to wine, such as *fuchsine*, *cochineal*, *logwood*, *litmus*, *beetroot*, *Brazil-wood*, *indigo*, etc., penetrate the gelatine to the centre of the cubes. Dilute ammonia will dissolve from the stained cake the colouring matter of *logwood* and *cochineal*. *Alkanet* is the only colouring matter in general use which resembles the natural colouring of wine, in the slow rate in which it diffuses into the jelly, hence if no coloration of the interior of the jelly be observed, *alkanet* is the only foreign colouring matter likely to be present. Ammonia changes the red colouring matter of *alkanet* root to a beautiful blue.

A test in use in the Paris Municipal Laboratory is as follows: A few drops of the wine are dropped on to a piece of recently calcined lime; the following colours are stated to be produced: *Natural red wine* gives a yellowish-brown coloration; wine coloured with *fuchsine* or *Brazil-wood* gives a rose colour; wine coloured with *logwood* gives a reddish-violet colour.

If ammonium hydroxide be added to the suspected sample of wine till a distinct alkaline reaction is obtained, then a little ammonium sulphide, and the liquid filtered, the filtrate from genuine wine will possess a green tint, whereas that obtained from artificially coloured wine will exhibit other colours, such as red, violet, brown, etc.

Logwood may be detected as follows: 20 cc. of the sample is well shaken with about 2 grammes of finely-powdered manganese dioxide, and treating the filtered liquid with zinc and hydrochloric acid, which destroys the brown coloration of the oxidized logwood. The colourless and neutralized liquid, if logwood be present, gives a red-violet colour with lime water, and a violet with ammonium molybdate in a solution slightly acid with nitric acid.

Rosaniline salts (*fuchsine* and *magenta*) may be detected according to A. H. Allen by rendering 50 cc. of the wine slightly alkaline with ammonia, and boiling the

liquid with a little white wool till all the alcohol and ammonia are expelled. The wool is then removed, washed, and at once heated with a few drops of solution of soda till dissolved. After cooling, about 5 cc. of water and the same measure of alcohol are added, and the liquid is shaken with 10 cc. of ether. On separating the ethereal layer and adding to it a drop of acetic acid, a red or pink colour will be developed if a mere trace of rosaniline be present. For the detection of a somewhat larger quantity, it is sufficient to render the wine alkaline with ammonia, agitate with ether, and shake the separated ethereal solution with dilute acetic acid, when a red coloration will be produced.

For the detection of *aniline colours* in wines and fruit-juices, etc., C. O. Curtman (*Zeitschr. f. Anal. Chem.*, H. 4) has published the following test, dependent upon Hofmann's isonitril reaction: To 4 cc. of the wine are added 4 cc. of potash solution and 2 drops of chloroform. After first gently warming and subsequent boiling, the characteristic smell of isonitril is plainly perceptible. The *sulpho-compounds of rosaniline* give the reaction only after some time. The test may be rendered more delicate by finally adding a little sulphuric acid. The small quantities of compound ethers present in the wine do not interfere with the delicacy of the test. The test is also successful with *aniline blue*, *purple*, *violet*, *magenta*, *red*, and many *yellow* and *green aniline colours*.

Preservatives.—Both salicylic and boric acids are frequently added to wine to prevent after-fermentation.

Salicylic Acid.—This is detected as given under 'Beer,' or by the following test devised by Curtman (*Jour. Pharm.*, xiv. 523): To 4 cc. of the wine (or beer) is added 2 cc. of methyl alcohol and 2 cc. of sulphuric acid. Shake the mixture, heat gently for two minutes, then allow to cool. Next heat to boiling, when, if salicylic acid is present, the odour of oil of wintergreen (methyl salicylate) will be perceptible.

Boric Acid.—Test the ash of the wine by the flame coloration test as directed under 'Milk.' Boric acid is stated by many anthorities to be a normal constituent of wine. Recently Professor Rising, of San Francisco, found it to exist in traces in Californian wines, whilst Ripper found it in 1,000 samples of German and other wines.

G. Baument (*Berichte*, December 10, 1888) found traces of boric acid to be present in a large number of genuine French, German, and Spanish wines.

Saccharine (*Benzoyl Sulphonic-imide*).—Extensive use of this sweetening agent is made on the Continent. It can be detected by Schmitt's process as given under 'Beer.'

The following are some of the conclusions arrived at by a commission appointed by the German Government to inquire into uniform methods for wine analysis, and to establish standards of purity :*

(*a*) After deducting the non-volatile acids, the extract in natural wine should amount to at least 1·1 grammes per 100 cc. ; after deducting the free acids, to at least 1 gramme per 100 cc.

(*b*) Most natural wines contain 1 part of ash to 10 parts of extract.

(*c*) The free tartaric acid should not exceed one-sixth of the total non-volatile acids.

(*d*) Genuine wines seldom contain less than 0·14 gramme of ash, nor more than 0·05 gramme of sodium chloride per 100 cc.

At the Paris Municipal Laboratory the following standards are adopted : The amount of added water in all wines, not sold as of a special or abnormal character, is calculated on a basis of 12 per cent. of alcohol (by volume), and 2·4 per cent. of extract.

The proportion of potassium sulphate must not exceed in unplastered wines 0·06 per cent. The use of preservatives is prohibited.

R. Borgman gives the following average relations of the various constituents of pure wine :

Alcohol	: Glycerine	=	100 : 10·5
Extract	: Acidity	=	1000 : 16·6
Acidity	: Ash	=	10 : 3·4
Ash	: Extractives	=	1 : 11·2
Phosphoric acid	: Ash	=	1 : 6·8

From the investigations of Dr. Dupré, it would appear that in genuine unfortified wines the amount of alcohol varies from 6 to 12 per cent. Fortified wines, in which

* *Reichsanzeiger*, 1884, No. 154.

fermentation has been checked by the addition of alcohol, often contain 5 per cent. of sugar ; champagnes usually show from 4 to 10 per cent. of sugar.

Analyses of Typical Wines obtained by Various Authorities.

	Specific Gravity at 15·5° C.	Alcohol Percentage by Weight.	Extract.	Sugar.	Ash.	Phosphoric Acid as P_2O_5.	Fixed Acid as Tartaric.	Volatile Acid as Acetic.	Real Tartaric Acid.
Red French ...	—	8·5	2·4	—	0·25	0·30	—	—	—
Red French ...	·9950	12·0	2·4	0·2	0·22	0·05	0·42	0·17	0·18
White French	—	9·4	2·5	—	0·26	0·30	—	—	—
White French	·9920	10·8	1·3	0·9	0·20	0·03	0·43	0·17	0·10
Vin Ordinaire	—	7·0	5·0	0·1	0·45	—	0·61	0·11	—
St. Julien ...	—	9·8	2·7	0·3	0·40	0·08	0·51	0·14	—
Champagne ...	—	7·9	12·4	10·6	0·30	0·05	—	—	—
Rhenish ...	·9934	9·2	1·9	0·1	0·20	0·03	0·42	0·11	0·25
Moselle ...	—	8·0	2·1	—	0·22	0·05	—	—	—
Hock	—	8·8	2·3	—	0·20	0·04	—	—	—
Sherry ...	·9979	17·2	5·3	3·0	0·50	0·20	0·52	—	—
Sherry ...	·9940	17·2	4·2	2·5	0·40	0·02	0·27	0·15	0·18
Port	·9974	17·5	5·4	2·3	0·30	0·03	0·50	—	—
Port	·9869	18·3	3·1	1·0	0·20	0·03	0·40	—	—
Port	1·1004	18·5	7·5	4·3	0·30	0·05	0·31	0 08	0·22
Madeira ...	·9939	16·7	5·0	2·1	0·40	0·04	0·54	—	—
Marsala ...	·9966	17·5	5·4	3·2	0·20	0·02	0·32	—	—
Greek... ...	·9931	13·9	2·5	0·4	0·40	0·04	0·23	0·18	0·30
Hungarian ...	·9921	8·5	1·8	0·0	0·20	0·02	0·53	0·15	0·07
Californian ...	—	10·4	2·1	0·0	0·20	0·02	0·48	0·08	—
Californian ...	—	9·8	2·1	0·1	0·20	0·02	0·41	0·10	—

SPIRITS.

Spirits are liquids prepared by distilling alcohol containing liquors. Various grains, such as wheat, Indian corn, barley, fruit-juices, etc., may be made to yield alcoholic

liquids by fermentation. When the alcoholic liquid so obtained is distilled, the distillate constitutes a 'spirit.'

Brandy.—Cognac, or French brandy, is prepared by the distillation of wine. An inferior variety is made from the 'marc' of grapes, consisting of the skins and stalks. The characteristic taste and bouquet of the original wine are to a considerable extent communicated to the resulting brandy, and on these qualities its value depends. 'British' brandy is manufactured from grain spirit, flavoured with ethyl acetate, nitrite, etc., oils of cassia, cloves, tincture of allspice, capsicum, etc.

When brandy is first distilled it is colourless, its amber tint being due to the casks in which it is stored. The constituents of brandy are water, alcohol, traces of various ethers, aldehydes, and acids, chiefly acetic. The specific gravity is usually about ·930. Total solids about 1·0 per cent.

Whisky. — Whisky is prepared from grain, mostly barley, both malted and raw. The distillation of this spirit is largely carried on in Scotland and Ireland. The smoky flavour of whisky is due to the fact that the malt used has been dried in kilns in which peat has been used for fuel. Whisky usually contains a trace of free acid, but this rarely exceeds 0·1 per cent. as acetic acid. Whisky when first distilled is colourless, but by storing in sherry casks, the usual method employed to give flavour, it acquires colour, and takes up traces of sugar, tannin, etc. The total solids rarely exceed 0·15 per cent.

Rum.—Rum is obtained by the distillation of the fermented juice of the sugar-cane or molasses. The distillation is carried on in the West Indies, North America, etc., but a great deal of this article is made from grain spirit, flavoured with various ethers and essential oils. The characteristic odour of rum is due to ethel butyrate. The specific gravity ranges from ·874 to ·926 ; alcohol from 50 to 70 per cent. ; total solids from 0·7 to 1·5 per cent.

Gin is a spirit originally prepared from grain, flavoured with juniper-berries, oil of juniper, coriander-seeds, turpentine, capsicum, etc., with or without the addition of cane-sugar. Hollands and Schnapps are varieties of gin.

Analysis of Spirits.

The most frequent form of adulteration of spirits is the addition of water. The alcoholic strength and total solids

should be determined. Methylic alcohol should be tested for, also fusel oil, to which may be traced the detrimental physiological effects of unmatured spirits. The keeping of spirits in wood greatly improves them, owing to the conversion of the fusel oil into other bodies. Caramel (burnt sugar) is added to spirits for colouring purposes. It may be detected by its bitter taste, and the reducing power it exerts on Fehling's solution.

Alcohol.—This is determined by direct distillation, as directed under 'Beer.' It is best to dilute the sample with an equal bulk of water before distilling, to guard against loss of alcohol caused by distilling too concentrated a liquid. By the Sale of Food and Drugs Amendment Act of 1879, the minimum limit of strength for brandy, whisky and rum was fixed at 25° under proof (= 75 per cent. of proof spirit). For gin the limit was fixed at 35° under proof (= 65 per cent. of proof spirit).

Methylic Alcohol.—This is detected by the Riche and Bardy test. (See under 'Compound Tincture of Camphor.')

Fusel Oil (*Amyl Alcohol*) is best detected as follows: About 100 cc. of the spirit is very slowly distilled at a low as possible temperature to distil off the greater part of the alcohol. The residue in the flask is cooled and extracted with ether. If the separation does not take place spontaneously add an equal bulk of water. The ethereal solution is then allowed to evaporate at the ordinary temperature. To portions of the residue are applied the following tests: (*a*) Heat with sulphuric acid and a little potassium bichromate. The odour of valerianic acid is evolved if fusel oil is present. (*b*) Warmed with about double its volume of concentrated sulphuric acid: a violet-red colour is produced, and amyl-sulphuric acid is formed. (*c*) Heated with sulphuric acid and acetate of soda, the odour of jargonelle pear (*acetate of amyl*) is evolved.

The quantitative determination of fusel oil is by no means an easy matter. A very ingenious process has been devised by Marquardt.* The method is based on the extraction of the fusel oil by chloroform, the oxidation of the amylic alcohol to valeric acid, the conversion of the latter to barium valerate, and the estimation of the barium thus combined.

* *Berichte*, 1882, pp. 1370, 1661.

A. H. Allen, who has investigated this process, recommends the following procedure :

150 cc. of the sample is diluted with water to a specific gravity of about ·980, and agitated with 50 cc. of pure chloroform for a quarter of an hour. The aqueous layer is separated and shaken with another 50 cc. of chloroform, and subsequently treated a third time. The 150 cc. of chloroform, containing in solution the amylic alcohol of the spirit, is treated in a strong flask or bottle with 2 grammes of sulphuric acid and a solution of 5 grammes of potassium bichromate in 30 cc. of water. The flask is then closed, and kept at a temperature of 85° C., with frequent agitation, for six hours. The liquid is then distilled till all but 20 cc. have passed over, when 80 cc. of water is added to the residue, and the distillation continued till only 5 cc. remain in the flask. The distillates are digested for half an hour with barium carbonate, in a flask fitted with an inverted condenser, after which the chloroform is distilled off and the aqueous liquid evaporated to a volume of 5 cc. The solution is then filtered from the excess of barium carbonate, and the filtrate evaporated to dryness at 100° C. The residue ('A') is weighed, dissolved in water, and the solution diluted to 100 cc. ; 50 cc. of the solution is acidulated with nitric acid and precipitated by silver nitrate, the resultant silver chloride being collected, weighed, and calculated into its equivalent of chlorine (143·5 of AgCl=35·5 of Cl). The remaining 50 cc. is precipitated with dilute sulphuric acid, the barium sulphate being collected, washed, and weighed. The weight found is calculated into its equivalent of barium (233 of $BaSO_4$=137 of Ba). The sum of the weights of the barium and chlorine found, subtracted from that of the residue ('A'), gives the weight of the valeric radicle contained therein, and this multiplied by the factor 0·871 gives the weight of amylic alcohol in the 150 cc. of spirit employed for the operation. The errors produced by the presence of substances in the fusel oil other than amylic alcohol tend to compensate each other, and hence the results are very fairly accurate. The chloroform for this process is best prepared from chloral, as the ordinary kind, though it may not colour sulphuric acid, is apt to contain impurities, which yield valeric acid and other volatile

fatty acids by oxidation. It is always best to do a 'blank' experiment upon pure alcohol.

Spirits should never contain more than 0·1 per cent. amylic alcohol.

POISONOUS METALS IN FOODS.

Tin, lead, and copper are occasionally found in foods, the latter being intentionally used to produce a brilliant colour in preserved peas and pickles.

Attention was first drawn to the fact that tin was often present in canned foods by E. A. Menke in 1878 (*Chem. News*, xxxviii. 971). In 1880 Otto Hehner (*Analyst*, v. 218) examined a considerable number of canned foods, both fruit, vegetables, and meats.

He also found tin in mineral water supplied in syphons.

In 1883 W. Blyth found tin in twenty-one samples of canned fruit, in amounts varying from 1½ grains to 11 grains per lb., with a mean of 4·5 grains. He considered the action mainly due to the acid juices of the fruit.

Dr. F. L. Teed (*Analyst*, xvii. 142) read a paper on the detection and estimation of small quantities of lead in presence of copper and iron. These three metals often occur together in aërated beverages. Dr. Teed takes advantage of the fact that sulphide of copper is soluble in potassium cyanide, while sulphide of lead is not. The liquid to be tested is placed in a cylinder, and a few cc. of ammonia and a little potassium cyanide added, and then a small quantity of ammonium sulphide. Any coloration produced is due to lead, copper and iron not interfering. This method is of especial value when the ordinary method of precipitating lead as chromate cannot be employed, as in liquids containing tartaric and other vegetable acids or organic matter, which have a reducing action of potassium bichromate.

Aërated water *not* supplied in syphons may contain lead, and different bottles often contain varying amounts, so that when samples are taken, if three bottles are purchased they should be opened, mixed in a jug, and poured back into bottles and sealed up.

In testing *drinking waters* for lead, the most convenient plan is to place 100 cc. of the sample in Nessler glasses

and pass sulphuretted hydrogen till the liquid smells strongly of it. If a dark colour is produced which does not disappear with a few drops of hydrochloric acid, it is due to lead (or copper), and can be confirmed by the potassium chromate method.

The tint produced by sulphuretted hydrogen is compared against standard solutions of lead acetate.

The delicacy of both these methods is very considerable, and in each case it is possible to detect $\frac{1}{50}$ grain per gallon of lead, provided that in the sulphide method the liquid is placed in a tall cylinder, and in the bichromate allowed to stand twelve hours till the precipitate has had time to settle.

Copper in Peas, Pickles, etc.—When copper alone is present, its amount may be estimated most conveniently by electrolysis.

A large quantity of the sample is ashed, and the ash treated with sulphuric acid, diluted, filtered, and made up to 40 cc., and transferred to a platinum crucible capable of holding 70 cc. The crucible stands on a piece of platinum foil connected to zinc of a single Grove's cell, while a platinum spatula is clamped so as to be in the centre of the liquid in the crucible, but not to touch its sides; the spatula is connected to the platinum of the battery. When charged and connected, the battery should be left to run all night.

It can be seen whether the current is passing by the minute bubbles of oxygen which rise from the platinum spatula.

In the morning the action should be complete, and if the liquid is free from copper (a single drop spotted on a tile failing to give a brown or black colour with sulphuretted hydrogen), the contents of the crucible are washed out with recently boiled distilled water, and then with spirit and ether, and dried a few minutes and weighed. The film should be coherent and brilliant in colour. This method is more exact than an estimation as sulphide of copper.

COMMERCIAL DISINFECTANTS.

Assays as regards the value of commercial disinfectants can only be made by chemical means in so far as the

determination of the percentage they contain of bodies on which their action depends, such as carbolic acid, metallic salts, etc.

Their actual efficiency—*i.e.*, power of killing disease-germs—can only be determined by bacteriological tests.

There are a great number of so-called disinfectants, concerning many of which very exaggerated claims are put forth ; some even contain amounts of caustic alkali, which would be harmful if applied to the skin according to the directions given.

It would be a great benefit to the general public if disinfectants were included under the Sale of Food and Drugs Acts, and such a course would prevent the sale of many useless and fraudulent preparations.

Disinfectants may be roughly divided into the following classes :

(*a*) Powders : carbolic and sulphite powders.

(*b*) Liquid disinfectants, depending on the action of carbolic or cresylic acids.

(*c*) Solutions of metallic salts.

Attention was drawn by Dr. Muter as far back as 1887 (*Analyst*, xii. 191), and again in 1890 (*Analyst*, xv. 63), to the fact that several of the so-called carbolic powders of commerce are practically devoid of carbolic acid, or contain it in a condition in which it cannot be reckoned as available.

Some powders contain sulphite of lime, as well as tar-products, and Dr. Muter considers that in estimating the amount 'reversion' should be allowed for.

The local authorities and their advisers are entirely to blame for the loss of life and waste of money occasioned by the supply of rubbish under the name of 'disinfectants,' and the condition of affairs can only be rectified by the adoption of a concise form of specification, and by the periodical sampling and analysis of the deliveries.

The following form of specification is a satisfactory one.

'*Tender for Supply of Carbolic Powder.*—The powder to contain not less than 15 per cent. of tar acids, *i.e.*, crude carbolic acid, of which 62½ per cent. crystallizes at 15° to 20° C., when examined by C. Lowe's test,' the base to contain no lime or chalk.

Assay of Carbolic Powders.—One or other of the two following methods may be adopted. The first is useful

in showing how much of the carbolic acid present can be considered available, while the second provides for its complete extraction.

1. The powder is well mixed, and 50 grammes are extracted with spirit ; this extracts all the tar acids not in combination with lime. The extract is mixed with 50 cc. of 10 per cent. solution of caustic potash or soda, and the spirit distilled off and the liquid evaporated to about 30 cc. If any tar oils separate out, they are filtered off. The liquid is then run into a burette, and 50 per cent. sulphuric acid added a little at a time till the soda is completely neutralized. The tar acids are thus 'thrown up,' and will form a separate layer, the volume of which may be read off. On multiplying the number of cc. thus obtained by 2, we shall get the percentage of phenols and cresols present.

2. This method is applicable to powders which give an alkaline reaction to litmus, showing that they contain free lime. The method of procedure is as follows :

50 grammes of the carefully-sampled powder is placed in a large mortar, and a cold mixture of equal parts—sulphuric acid and water—added drop by drop, the powder being stirred thoroughly meantime till all the lime has been converted into sulphate, as is indicated by a fragment of the powder no longer producing a blue spot with a drop of water on red litmus paper.

The operation should be extended over one hour, and the powder must not be allowed to grow hot, or there will be loss of carbolic acid through volatilization. If the operation has been well conducted, the powder will when neutralized be dry, and free from lumps. If it seems moist, anhydrous calcium sulphate should be added.

The powder is now extracted by four successive treatments with ether, as much ether as possible being poured off each time through a small filter into a flask containing 50 cc. of 10 per cent. sodium hydrate. The ethereal solution is then well agitated with the alkaline liquid, after which the flask is attached to a condenser, and the greater part of the ether distilled off.

The contents of the flask are now poured into a separator, and the flask washed out with small successive quantities of ether and water, which are, of course, poured into the separator. After well mixing by a rotary movement, the separator is set aside, and when the layers have separated

well, the lower is run out into a basin, and the upper washed once with water in the separator, the washing being also run into the dish. The ether layer contains any neutral tar-oils, which may be estimated if desired by distilling off the ether in a weighed flask.

The phenate and cresylates of soda in the dish are evaporated to 30 cc., transferred to a burette, and treated as described above.

If it is desired to ascertain how much *crystallizable carbolic acid* is present, we must extract a large enough quantity to yield at least 50 cc. of tar acids, which are then treated as described below :

Assay of Crude Carbolic Acid.—The object of this test is to ascertain the amount of crystallizable phenols contained in crude carbolic acid, and the temperature at which such crystallization occurs. The higher the temperature at which the selected portion of the distillate crystallizes, the better the sample.

Lowe's Test : 100 cc. of the sample are placed in a small retort, and heated by means of a small flame; no condenser is needed. The *rate* of distillation should be such that the drops follow each other rapidly, but do not fall in a continuous stream.

Two graduated cylinders are required, the first portion of the distillate—that is to say, all the water and 10 per cent. of the oils—being received into the first ; this is then exchanged for the other, and 62·5 cc. collected. This is poured into a flask, provided with a cork through which a thermometer passes ; and a fragment of phenol having been added, the liquid is gently stirred with the thermometer, and cooled. At the point of crystallization the thermometer rises slightly, and then remains constant. It is then read, and the temperature compared with those of mixtures of known composition.

Liquid Carbolic Preparations.—There are several liquid preparations, whose efficacy depends chiefly on the amount of carbolic and cresylic acid they contain. Some of these are of the same type as the preparations sold as sheep-dips, and form very perfect emulsions with water.

They are prepared by heating rosin with caustic soda, and then stirring in tar oils while the mixture is kept hot. They may be assayed by throwing up the tar acids with 50 per cent. sulphuric acid, and then distilling the tar acids as in the assay of crude carbolic acid.

Solutions of Metallic Salts.—Solutions of the following are used as 'disinfectants': *Zinc chloride*, sometimes known as *Burnett's fluid; permanganates of soda and potash*, 'ozonigen' and Condy's fluid; *iron salts*, especially the sulphate; *mercuric chloride and iodide.*

The Local Government Board, in one of their memoranda, advise the use of a solution prepared with—½ oz. mercuric chloride, 1 oz. hydrochloric acid, 3 gallons of water, 5 grains aniline blue. This gives a solution of 1 in 980.

Bleaching-powder, in solution of 6 oz. to 1 gallon, is a very powerful and economical disinfectant. Of the above-mentioned preparations, mercuric chloride, permanganates of the alkali metals, and bleaching powder, are chiefly to be commended as having a true germicidal action. Iron and zinc salts are properly antiseptics and deodorants only.

THE EXAMINATION OF OILS AND FATS.

Animal and vegetable oils and fats are salts of glycerol with organic acids, or more correctly are 'mixtures of ethereal salts formed from glycerol and the fatty acids of the acetic and oleic series.'

The analysis of oils and fats requires great manipulative skill, and the interpretation of the results of analysis can only be successfully undertaken by those who have undergone a special training in this branch of work. There are great difficulties to contend with in the analysis of oils, many of which, of very different market values, are exceedingly similar in chemical constitution; many samples of the same oil may vary amongst themselves. The fatty acids on which the main differences depend cannot be readily separated or caused to enter into definite weighable compounds. Oils vary greatly in value, and hence there exists a constant inducement to adulterate the more valuable ones with those of an inferior kind. It must be borne in mind that, like other natural productions, oils vary very much according to the place of production, method of manufacture, purification, etc. It cannot be too strongly insisted upon that a given sample should not be pronounced as adulterated without comparing it with samples of known purity and origin.

In this small work we will only deal with the analytical constants of a few of the oils and fats in common use.

In the examination of an oil to ascertain its purity and

freedom from adulteration, it is necessary to examine it by the following tests :

The Specific Gravity is taken at 15·5° C. by the specific gravity bottle or the Westphal balance. In the case of oils or fats which are solid at the ordinary temperature, the specific gravity is taken at 99° C. by the Sprengel tube or Westphal balance. (See under 'Butter,' p. 26.)

The Saponification Equivalent (Koettstorfer's Method).—The saponification of oils by alkalies is a definite reaction which may be represented by the following general equation :

$$C_3H_5(O\bar{F})_3 + 3KHO = C_3H_5(OH)_3 + 3KO\bar{F}.$$

Therefore if we know exactly the amount of alkali necessary to saponify the oil under examination, we can to some extent determine the nature of the glycerides present. The saponification value varies with the composition of the fatty acids ; for instance, the lower the molecular weight of the fatty acids, the higher will be the amount of potash or soda necessary for the saponification. The saponification value of an oil may be stated in terms of alkali absorbed per cent., or the number of grammes of the oil which would be saponified by one litre of normal solution of alkali, which is usually known as the 'saponification equivalent.'

The following are the saponification values of some of the chief glycerides :

Glyceride.	Formula.	Molecular Weight.	Percentage of KHO required for Saponification.	Saponification Equivalent.
Butyrin	$C_3H_5(O{\cdot}C_4H_7O)_3$	302	55·7	=100·67
Laurin	$C_3H_5(O{\cdot}C_{12}H_{23}O)_3$	638	26·4	=212·67
Palmitin	$C_3H_5(O{\cdot}C_{16}H_{31}O)_3$	806	20·9	=268·67
Stearin	$C_3H_5(O{\cdot}C_{18}H_{35}O)_3$	890	18·9	=296·67
Olein	$C_3H_5(O{\cdot}C_{18}H_{33}O)_3$	884	19·0	=294·67

From the above table it is seen that the amount of alkali required for the saponification of the various glycerides differs largely. Since oils are mixtures of different glycerides, the ratio of which within certain limits is usually constant for the same class of oil, it will be seen that this process becomes very valuable in the examination of oils and fats. The process is carried out as follows : About 2 grammes of the sample is accurately

weighed out in a flask of about 200 cc. capacity. This is then treated with 25 cc. of alcoholic solution of caustic potash of approximately semi-normal strength.* A like amount of the alkali is run into an empty flask for a blank experiment. It is not necessary that exactly 25 cc. be taken, but precisely the same quantity must be taken in each case. A good plan is to let the pipette empty, and then allow three or four drops to fall; this will ensure the same amount of solution being taken in each case. The flasks are fitted with corks carrying vertical tubes about 4 feet long, to act as condensers. Both the flasks are then heated on a water-bath for not less than thirty minutes, with frequent agitation. One or two drops of phenolphthalein are added to the flasks, the contents of which are titrated with exactly $\frac{N}{10}$ solution of hydrochloric acid. Each cc. of $\frac{N}{2}$ HCl used = ·02805 of KHO, therefore the difference between the two titrations multiplied by this factor will give the amount of potash taken up by the oil, and from this is calculated the percentage of alkali required for saponification.

The saponification equivalent is found from the percentage of KHO absorbed by dividing into 5610. It can also be obtained by dividing the weight of oil taken in milligrammes by the number of cc. of normal alkali required for its saponification.

Example—

Amount of oil taken 2·001 grammes.

$\frac{N}{2}$ HCl for titrating back	12·2 cc.
$\frac{N}{2}$ HCl required for 'blank'	26·0 cc.
Difference =	13·8 cc.

$$13{\cdot}8 \times {\cdot}02805 = \frac{{\cdot}38709 \times 100}{2{\cdot}001} = 19{\cdot}3\ \%\ \text{KHO} = \frac{5610}{19{\cdot}3}$$

$$= 290 \text{ saponification equivalent.}$$

Determination of the Unsaponifiable Matter.—5 grammes of the sample is saponified with 50 cc. of alcoholic potash of approximately semi-normal strength, by boiling under a reflux condenser for about thirty minutes, with frequent agitation. The solution is then evaporated

* This is best made by taking about 60 grammes of 50 per cent. solution of caustic potash and diluting to a litre with 'methylated spirit' which has been redistilled from ignited potassium carbonate.

down to dryness in a dish. The resulting soap is dissolved in about 200 cc. of hot water ; when dissolved, the solution is transferred to a separator, which is immersed in cold water to allow the contents to cool. The aqueous solution of the soap is then treated with about half its volume of ether, the stopper inserted, and the whole thoroughly shaken and allowed to rest some time. It sometimes happens that the ether will not separate from the soap solution, a middle layer of gelatinous consistency being formed. In this case separation may be induced to take place by well cooling the separator under a stream of water, or, if this fails, by adding a few cc. of 10 per cent. potash solution, and a little more ether ; separation is assisted by giving a rotary motion to the separator. The ethereal layer is separated, and the soap solution again extracted with ether, repeating the treatment again if necessary. The ethereal solutions are mixed, and well shaken up with water to wash out any soap which may have been taken up into the ether. The ether solution is separated, transferred to a flask, the ether distilled off, and the residue dried at 105° C. to constant weight, which multiplied by 20 will give the percentage of unsaponifiable matter present in the oil.

Nature of the Unsaponifiable Matter.—This may consist of cholesterol, phytosterol, mineral oil (hydro-carbons), rosin oil, etc. If the amount does not exceed about 1 per cent., it probably consists of cholesterol or phytosterol. These are higher alcohols of crystalline character and high melting-point which occur in small quantity in animal and vegetable oils respectively. Hydro-carbons, such as heavy mineral oil, may often be detected by the fluorescence which is imparted to the ethereal solution. Rosin oil, if present, may be detected by the bromide of tin test. (See under 'Colour Tests.')

Hubl's Iodine Absorption Equivalent.—This method, devised by Hubl, is based on the fact that all oils and fats are composed of the glycerine ethers of the members of two groups of fatty acids—the acetic and oleic series. The relative proportion of these acids in any variety of oil or fat is constant within certain limits, and differs only in different kinds of oil, but the members of the two groups of acids exhibit a very different behaviour towards chlorine, bromine, and iodine. While under ordinary circumstances the acids of the acetic series are indifferent, those of the

oleic series readily unite with definite quantities of the halogens. If, therefore, it is possible to make a fat or oil unite with a halogen, so that the amount of the latter which enters into the compound may be accurately determined, the number thus obtained would be a constant, and would be dependent upon the amount of unsaturated acids in the oil. Some chemists estimate the bromine absorption, but Hubl's iodine process is more convenient, and is the one we will describe here.

The Hubl solution is made as follows: 25 grammes of iodine is dissolved in 500 cc. of 95 per cent. alcohol, and 30 grammes of mercuric chloride in the same amount of alcohol. These two solutions are then mixed together, and allowed to stand at least twelve hours before using.

The determination is made as follows: About 0·2 to 0·35 gramme of the sample is accurately weighed by difference into a stoppered bottle of about 250 cc. capacity. The oil is then dissolved in 10 cc. of chloroform; when this has taken place, 25 cc. of the Hubl reagent is added from a pipette. A blank experiment is also started, using the same quantity of chloroform and iodine solution. The bottles are then allowed to remain in the dark for not less than four hours. To the contents of the bottle is then added 20 cc. of a 10 per cent. solution of potassium iodide and about 150 cc. of water. The uncombined iodine is then titrated with $\frac{N}{10}$ sodium thiosulphate solution, the bottles being violently agitated during the titration until the free iodine has nearly disappeared, when a little fresh starch paste is added, and the thiosulphate added drop by drop, until the blue colour is just discharged. The number of cc. of thiosulphate used is deducted from the amount required for the blank experiment; the difference is multiplied by ·0127 (if the thiosulphate is exactly decinormal). This gives the amount of iodine taken up by the oil, and from this is calculated the percentage of iodine absorbed.

Example—

Oil taken 0·205.
Blank experiment required 30·0 cc.
Thiosulphate required 18·0 cc.

Difference = 12·0 cc. × ·0127 =

$$\frac{\cdot 15494 \times 100}{\cdot 205} = 75\cdot 6 \text{ per cent. } \textit{iodine absorbed.}$$

The thiosulphate solution must always be standardized before using against pure iodine to ascertain its exact strength.

Free Fatty Acid.—Animal oils, when first prepared, and the first runnings in the case of oils of vegetable origin, contain only traces of free fatty acids. On exposure to air, however, the free fatty acid increases rapidly, the result being that the oil becomes rancid. The lower grades of vegetable oils generally contain a large percentage of free fatty acid, often amounting to 30 or more per cent. The determination is made as follows: 5 or 10 grammes of the oil is well shaken with about 100 cc. of boiling neutral alcohol. A drop or two of phenol-phthalein solution is added, and decinormal solution of NaHO run in with constant agitation, until a permanent pink colour is obtained. Each cc. of $\frac{N}{10}$ NaHO = ·0282 oleic acid. Oils intended for dietetic purposes should not have a greater rancidity than 4 or 5 per cent. of free fatty acid calculated as oleic.

Maumené's Test.—This test depends on the rise of temperature which takes place on mixing oils with concentrated sulphuric acid. Much work has been done on this process by various chemists, who have arrived at very opposite opinions regarding its value as a quantitative test. Many of the discrepancies which are found between the results of many of these observers are in great measure due to the different methods of working, and also to the variation in strength of the sulphuric acid employed. Allen and Archbutt, who have carefully investigated this test, find that if the strength of the acid is much below 97 per cent. the temperature attained is not only less, but the reaction is much slower. Other workers have advised the use of 93 and 95 per cent. acid respectively, but these strengths are not to be recommended. The acid which gives the best results is 97 per cent. The strength of the acid must be determined by careful titration, as the specific gravity is quite useless to determine the strength of sulphuric acid, as Lunge has shown that acid of 95 to 100 per cent. may have almost exactly the same specific gravity. The following is the best procedure for the carrying out of this test:

50 grammes of the sample is weighed out into a tall beaker of about 250 cc. capacity; this is wrapped in cotton-wool, which is encased in a suitable box or larger beaker.

The temperature of the oil, which should be at about 18° to 20° C. is carefully noted; 10 cc. of the 97 per cent. H_2SO_4 is then run from a pipette into the beaker containing the oil, the mixture being constantly stirred with the thermometer; the rate of flow of the acid should be so arranged that the delivery of the 10 cc. takes about sixty seconds. The stirring is continued until the temperature ceases to rise; this point is readily observed, as the temperature generally remains constant for some short time before falling. The temperature of the acid should be about the same as the oil, but this is not of very great importance, since E. J. Bevan has found that 5° difference of temperature between that of the oil and acid does not influence the result.

The initial temperature of the oil is deducted from the highest reached after the addition of the acid, and the difference noted as the 'temperature reaction' of the oil.

Messrs. Ballantyne and Thomson have suggested a modified form of the Maumené test, wherein the temperature is compared with that of water under the same conditions. The rise of temperature observed with the oil is divided by that given by water; the figure so obtained he calls the 'specific heating power' of the oil.

The Maumené test should be done in a draught cupboard or in the open air, as in some cases a large volume of sulphur dioxide is given off.

Valenta Acetic Acid Test.—This test has given in our hands such satisfactory results in the examination of oils that we are surprised that it has not held a more important position than it appears to have done. The test, as we have before mentioned, depends on the intermiscibility of the glycerides with acetic acid at various temperatures. (For method of performing test see under 'Butter.')

A somewhat improved method of working this test is, instead of using an ordinary test-tube, to use a short and somewhat thick tube into which a well-fitting stopper has been ground. Into this tube is weighed 2·75 grammes of the fat; 3 cc. of the acetic acid is then run in from a burette or other suitable arrangement. The tube is then stoppered and placed in a beaker of warm water, increasing the heat until, after well shaking the tube, the contents become quite clear. The source of heat is then removed, and the test-tube so placed that it is in the centre of the

beaker of heated water, and by means of a thermometer attached to the tube by a rubber band the whole is allowed to rest until the change from brilliancy to turbidity. The change is very definite, and can be repeated over and over again with a maximum error of about 0·25° C.

The Oleorefractometer.—See the description and method of working this instrument under 'Butter.'

Colour Tests.—Many colour tests have been suggested from time to time, dependent on the fact that many oils yield colour reactions when treated with various reagents, such as sulphuric acid, nitric acid, mercurous nitrate, stannic chloride, etc. Many of these tests are not dependent on the oils themselves, but on impurities contained therein, such as albuminous and resinous substances. As these matters are now largely removed by the improved processes of purification and refining used, it follows that very considerable variation must be observed in the behaviour of different samples of the same oil to these reagents. These tests are therefore of little value, so no description of them will be given here.

A colour reaction, to be of value, must depend for its reaction on the oil itself, or on a substance contained in and natural to the oil. To this class belong the Baudouin and Tocher tests for sesame-oil, the silver nitrate test for cotton-seed-oil, the bromide of tin test for rosin oil, and the Hager test for cholesterol.

Hager's Test for Cholesterol.—A small fragment of cholesterol is dissolved in about 2 cc. of chloroform, and an equal volume of strong sulphuric acid added. The chloroformic solution immediately becomes blood-red, afterwards purple, which remains permanent for some days, while the acid layer shows a strong green fluorescence. Phytosterol gives the above reaction, but the chloroformic solution becomes bluish-red after a day or two.

The Bromide of Tin Test for Rosin Oil.—Stannic bromide, containing a little free bromine, is dissolved in carbon disulphide. When a drop or two of this reagent is added to rosin oil, a beautiful violet colour appears.

The stannic bromide is made by allowing dry bromine to drop on granulated tin contained in a flask until a red coloration of the product indicates that bromine is in excess.

This test may be applied to the unsaponifiable matter to determine the presence or absence of rosin oil.

Analytical Constants of Oils and Fats.

	Oil or Fat.	Sp. Gr. at 15·5° C.	Percentage KHO for Saponification	Iodine Absorption.	Valenta Test.	Oleorefractometer Figure.	Maumené Test.
	VEGETABLE OILS.						
Non-drying Oils.	Olive	·914 to ·917	19·0 to 19·6	77·0 to 86·0	83° to 91°	+ 3·5 to 1·0	40° to 45°
	Almond	·916 to ·920	19·5 to 19·7	94·0 to 99·0	72° to 87°	+10·5 to 8·0	51° to 54°
	Peach-kernel ...	·918 to ·921	18·9 to 19·2	95·0 to 99·5	80° to 83°	+11·5 to 7·5	40° to 46°
	Arachis	·917 to ·921	19·0 to 19·6	95·0 to 102·0	72° to 74°	+ 7·0 to 5·0	45° to 60°
Semi-drying Oils.	Cottonseed ...	·922 to ·930	19·1 to 19·7	101·0 to 116·0	71° to 89°	+23·0 to 16·0	74° to 80°
	Sesame	·923 to .924	18·8 to 19·1	106·0 to 108·0	90° to 97°	+17·0 to 13·0	64° to 68°
	Rape	·914 to ·917	17·5 to 17·8	99·5 to 105·5	77° to 83°	+20·0 to 16·0	52° to 59°
	Castor	·960 to ·966	17·8 to 18·0	83·6 to 83·9	Miscible.	+42·0 to 39·0	45° to 47°
	Mustard ...	·916 to ·920	17·2 to 17·5	92·0 to 100·0	—	—	44° to 49°
Drying Oils.	Linseed	·932 to ·937	18·7 to 19·5	173·5 to 187·7	46° to 48°	+54·0 to 48·0	104° to 120°
	Hempseed ...	·925 to ·931	19·0 to 19·3	144·0 to 150·0	—	+37·4 to 34·0	95° to 98°
	Nigerseed ...	·927 to ·930	18·9 to 19·1	132·0 to 135·0	50° to 53°	+30·0 to 26·0	81° to 83°
	Sunflower ...	·924 to ·926	19·3 to 19·4	122·0 to 133·0	59° to 63°	+35	67° to 75°

Analytical Constants of Oils and Fats.—*Continued.*

Oil or Fat.	Sp. Gr. at 15·5° C.	Percentage KHO for Saponification	Iodine Absorption.	Valenta Test.	Oleorefractometer Figure.	Maumené Test.
ANIMAL OILS.						
Neat's foot ...	·914 to ·916	19·4 to 19·6	69·3 to 70·4	72° to 75°	− 3·0 to 1·0	47° to 49°
Lard oil ...	·914 to ·916	19·1 to 19·6	77·0 to 80·0	74° to 76°	Zero.	65° to 67°
FISH OILS.						
Cod-liver ...	·923 to ·930	18·2 to 18·7	141·0 to 144·0	70° to 76°	+46·0 to 40·0	113° to 116°
Whale	·919 to ·931	18·8 to 22·4	81·0 to 110·0	68° to 71°	+48·0 to 42·0	86° to 90°
Seal	·924 to ·929	18·9 to 19·3	142·0 to 153·5	70° to 75°	+36·0 to 30·0	90° to 95°
	Sp. Gr. at 99°C. Water=1.					
VEGETABLE FATS.						
Palm oil ...	858·5	19·6 to 20·2	51·0 to 52·5	—	—	—
Cotton stearin ...	864·8	19·5 to 19·6	89·0 to 92·0	—	—	—
Cacao butter ...	858·0	19·2 to 20·1	34·0 to 37·0	—	—	—
ANIMAL FATS.						
Butter fat ...	·865 to ·867	22·1 to 23·2	23·0 to 38·0	29° to 39°	−34·0 to 25·0	—
Margarine ...	·856 to ·860	19·3 to 19·7	50·0 to 57·0	94° to 97°	−18·0 to 13·0	—
Lard	·860 to ·862	19·5 to 19·7	50·0 to 63·0	97° to 99°	−14·0 to 8·0	—
Tallow	860·8	19·3 to 19·8	35·0 to 42·0	96° to 99°	−18·0 to 15·0	—

Olive Oil.

Olive oil is obtained by expression or extraction from the fruit of the olive tree (*Oleo Europæa sativa*). The colour of olive oil varies from almost colourless to deep yellow ; some varieties are green, due to dissolved chlorophyl.

The free fatty acid varies very much in different samples. In 'salad' oil it should not exceed 4 or 5 per cent., but in commercial samples it may be as high as 25 per cent. Olive oil gives the lowest mean rise of temperature in the Maumené test—40° to 45°. The unsaponifiable matter in olive oil averages about 1·0 per cent., and consists of cholesterol, whereas in other vegetable oils the unsaponifiable matter consists of phytosterol. Olive oil, on account of its high value, is adulterated to a very large extent. Cottonseed, arachis, poppy, rape, and sesame oils are among those used for its adulteration. Many of the bottled oils on the market sold as 'Finest Lucca Olive Oil,' and under other fancy names, consist entirely of cottonseed or arachis, or mixtures of these with a little olive oil.

The oleorefractometer is very useful in the examination of olive oil ; 120 samples examined gave the following results : Lowest deviation, +1·0 ; highest deviation, +3·5 ; average, +2·0.

The various oils used to adulterate olive oil would be detected as follows : Cottonseed oil by the high figures obtained with the iodine absorption, oleorefractometer, Maumené test and specific gravity, also by the silver test (see under 'Lard') ; arachis oil by the isolation of arachidic acid (see under 'Arachis' oil) ; sesame oil by the high iodine absorption, specific gravity, and oleorefractometer figures ; rape oil by the oleorefractometer, iodine absorption, Maumené and saponification tests.

Almond Oil.

Almond oil is expressed from the seed of the sweet and bitter almond-tree (*Prunus amydalus dulcis* and *Prunus amydalus amara*). Almond oil has a very pale yellow colour and bland taste. Almond oil is adulterated with

peach-kernel, olive, sesame, cottonseed, poppy, and arachis oils. Nearly the whole of the so-called 'foreign' almond oil consists of peach-kernel oil, the characters of which are, unfortunately, so similar to those of genuine almond oil that it is quite impossible to differentiate them by the quantitative tests. They can, however, be distinguished by their behaviour to nitric acid of specific gravity 1·40. Three parts of the oil is shaken with one part of the acid, when—Almond oil gives a light yellow colour, turning brown. Peach-kernel oil gives a bright red colour.

Cottonseed oil would be detected by the silver test, sesame oil by the Baudouin and Tocher tests.

Arachis Oil.

Arachis oil (pea-nut, earth-nut oil) is produced from the seeds of the leguminous plant *Arachis hypogœa*. The higher qualities, which are 'cold drawn,' have a pleasant taste, recalling kidney beans. Arachis oil has very similar analytical constants to olive oil, from which it cannot be detected except by the isolation of arachidic acid (see below). In chemical composition arachis oil is peculiar, as the glycerides olein and palmitin are replaced by the glyceride of arachidic acid. The isolation of this acid furnishes a very valuable method for determining the presence of arachis oil when used as an adulterant of other oils.

Determination of Arachidic Acid.—This is best done by the original method of Renard, which, though tedious, is very reliable. The process is carried out as follows: Saponify 10 grammes of the oil, separate the fatty acids from the soap solution by hydrochloric acid, dissolve these in 90 per cent. alcohol, and add a solution of lead acetate.* Filter off the precipitated lead salts, extract them with ether, thus separating the lead salts of the unsaturated acids from the lead palmitate and arachidate. Treat these latter salts with hydrochloric acid, separate the fatty acids when solidified, after cooling, from the lead chloride, and

* Lewkowitsch shortens the process by neutralizing the excess of alkali with acetic acid, and precipitating with a lead salt without isolating the fatty acid.

dissolve them in 50 cc. of hot 90 per cent. alcohol. If arachis oil is present in the sample, a crop of crystals consisting of arachidic acid will be obtained on cooling the alcoholic solution. Filter the crystals off, and wash them on the filter, first with a measured quantity of 90 per cent. alcohol, then with 70 per cent. alcohol, which dissolves but small quantities thereof, and finally dissolve them by pouring boiling absolute alcohol on the filter, receiving the filtrate in a tared dish or flask. Evaporate to dryness, and weigh the residue, consisting of crude arachidic acid. Add to the weight thus obtained the quantity dissolved by the 90 per cent. used for the washing, 100 cc. of which dissolve 0·022 gramme at 15·5°C., or 0·045 gramme at 20° C. Finally, determine the melting-point of the crude acid, which should be from 71° to 72° C. Renard has isolated from 4·5 to 5·0 per cent., A. H. Allen 5·5 per cent. of arachidic acid from oil of arachis. Hence the amount of acid found will represent approximately $\frac{1}{20}$ of the arachis oil present, and the latter may therefore be found by multiplying the weight of the acid by 20.

Sesame Oil.

Sesame oil (*Gingili oil, Teel oil*) is obtained from the seeds of the *Sesamum orientale* and *indicum*. The oil has a very pleasant taste, but little odour, and is generally of a light yellow colour. It belongs to the class of semi-drying oils. Sesame oil contains a very small quantity of a body upon the presence of which depend the two following characteristic colour reactions, known as the Baudouin and Tocher tests :

Baudouin's Test.—Dissolve 0·1 gramme of cane-sugar in 10 cc. of hydrochloric acid of specific gravity 1 2. To this is added 20 cc. of the oil to be tested ; shake thoroughly, and allow to stand. In the presence of even 2 per cent. of sesame oil the aqueous liquid will become of a crimson colour.

Tocher's Test.—1 gramme of pyrogallol is dissolved in 15 cc. of concentrated hydrochloric acid. This solution is well shaken in a separating funnel with 15 cc. of the oil, and allowed to stand. After separation has taken place, the aqueous liquid is drawn off and boiled for a few

minutes. If sesame oil is present, the solution becomes coloured, appearing red by transmitted, and blue by reflected, light.

Rape Oil.

Rape or colza oil is obtained by expression from the seeds of the *Brassica campestris*, and several allied plants belonging to the natural order Cruciferæ. In this country these oils are known indiscriminately as rape or colza oil. On the Continent, however, a distinction is drawn : the oil from the seeds of the *B. campestris* is known as colza ; the oil from the *B. campestris* var. *napus* is known as rape. Rape oil has a somewhat yellow colour and harsh, unpleasant taste. The oil belongs to the semi-drying class. The oil is extensively adulterated with linseed, hemp, cottonseed, fish, and mineral oils.

Castor Oil.

Castor oil is obtained from the seeds of the *Ricinus communis*. It is a colourless or greenish-tinged oil. It is very viscous, and thickens on exposure to air. It is entirely soluble in 1 volume of absolute alcohol, and in 4 volumes of rectified spirit. It is also miscible with glacial acetic acid in all proportions. Castor oil has the highest specific gravity of any natural fatty oil.

Linseed Oil.

Linseed oil is obtained by expression and extraction from the flax plant (*Linum usitatissimum*). The taste and odour are characteristic ; the oil obtained by hot pressure is sometimes very acrid and nauseous. Linseed is principally imported from the Baltic and Black Sea coast, also India. The Baltic seed yields the best oil. The colour of the cold-expressed oil is a bright golden-brown ; the hot expressed oil is very dark brown. On exposure to air linseed dries hard, absorbing oxygen, and forming a body insoluble in ether, known as linoxyn. Linseed has the highest iodine absorption and Maumené figure of all the fatty oils. On account of its cheapness, linseed is but seldom adulterated with other seed-oils, but rosin, mineral and fish oils are not unfrequently used as adulterants.

In the absence of any appreciable amount of unsaponifiable matter, any lowering of the iodine or Maumené figures would point to adulteration with fish-oils, as would also a low specific gravity.

Lard.

Lard is the internal fat of the abdomen of the pig. There are enormous quantities of lard rendered from the fat of the whole animal. According to Wiley, lards may be divided into the following classes :

(*a*) *Neutral Lard.*—This consists of the fat from the 'leaf' of the animal, rendered quite fresh at a temperature of from 40° to 45°. This lard is used in the manufacture of margarine.

(*b*) *Leaf or Bladder Lard.*—The fat of the 'leaf' rendered by steam heat under pressure.

(*c*) *Choice Lard, Kettle Lard, etc.*—This lard is generally rendered from the fat of the whole animal. According to the Chicago Board of Trade, choice lard is defined as lard made from the 'leaf' and trimmings, rendered by steam heat.

Freshly-rendered lard is quite free from free fatty acid. Lard possesses a pure white colour, a granular texture,and agreeable taste. The melting-point of lard is about 38° C. Lard is extensively adulterated with cottonseed oil, cottonseed and beef stearin. Many of the so-called 'compound' lards do not contain any lard at all, being mixtures of cottonseed oil and beef stearin. Arachis and sesame oils have been stated to have been used to adulterate lard ; they would be detected by Baudouin's and Tocher's tests.

The iodine absorption of pure lard will not be above 63 or below 50 per cent. If the iodine absorption falls out of this range, the sample must be considered as adulterated ; but the fact of a normal iodine figure being obtained does not prove the sample to be genuine, as a judicious mixture of cottonseed or arachis oil with cottonseed or beef stearin would give apparently normal figures when examined by the test.

The Silver Test for Cottonseed Oil.—This valuable test has received a great deal of attention at the hands of various chemists. There are many modifications of the

test in use. The following method will, in careful hands, detect as little as 1 per cent. of cottonseed oil. The reagent is made as follows : 1 gramme of finely-powdered nitrate of silver is dissolved in 100 cc. of 95 per cent. alcohol ; when dissolved, 20 cc. of ether and 1 drop of nitric acid are added ; 2 cc. of this reagent is well shaken with 10 cc. of the oil to be examined, and placed in boiling water for ten minutes. Any blackening due to reduced silver proves the presence of cottonseed oil.

Beef Stearin.—W. F. K. Stock has devised a method to determine the amount of beef stearin in lard. He compares the crystals obtained from an ethereal solution with those from two standard sets of mixtures, the first consisting of pure lard melting at 34° to 35° with 5, 10, 15, and 20 per cent. of beef stearin melting at 56° C. ; the second of pure lard, of melting-point 39° to 40°, with 5, 10, 15, and 20 per cent. of beef stearin melting at 50° C. The process is as follows : The melting-point of the sample is determined by the capillary-tube method. Suppose the melting-point be found at 34° C., 3 cc. of the melted fat are run into a graduated cylinder of about 25 cc. capacity ; 21 cc. of ether are added, and the fat dissolved at 20° to 25° C. ; 3 cc. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to 13° C., and allowed to remain at that temperature for twenty-four hours. An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of the deposited crystals. The ether is then poured off as far as possible, and 10 cc. of fresh ether at 13° C. is added in each case. The cylinders are again shaken, cooled as before, and the proportion of crystals read off as before. Finally, the contents of the cylinders are emptied into weighed shallow beakers, the ether drained off carefully, the mass allowed to dry for fifteen minutes at 10° C., and weighed. The weight obtained for the sample under examination is compared with the weight of the crystals obtained from whichever of the standards comes nearest to it. The second set of mixtures is used for samples of higher melting-point. The actual presence of beef fat must be proved by microscopical examination, when the characteristic tufts are seen if beef fat is present. No sample of pure lard melting below 39° C. yielded more than 0·011 gramme of crystals under the

above conditions. A sample of the melting point 45·8° C. gave, however, 0·146 grammes of crystals.

The following are some iodine absorption figures given by W. H. Wiley, United States Department of Agriculture (Bull. 13, p. 4):

Pure leaf lard (Squire and Co.) ...	56·9	per cent.
Pig's feet lard (Wesson and Co.) ...	77·3	„
Bladder lard (mean of 20 samples) ...	61·2	„
Steam lard (mean of 12 samples) ...	62·0	„
'Compound' lard (mean of 13 samples, Armour and Co.)	64·6	„
'Compound' lard (mean of 17 samples, Fairbank and Co)	85·3	„
Cottonseed oil (mean of 17 samples) ...	109·0	„
'Oleo' stearin (mean)	17·4	„
Lard stearin (mean)	44·2	„

Water.—Lard used to be very frequently adulterated by the introduction of water, but this sophistication is not now very frequent. Lard must be absolutely free from water and ash. The fat on melting should be clear, and free from suspended matter, such as particles of membrane, etc.

THE EXAMINATION OF SOAP.

The various kinds of soap in every-day use, for household or manufacturing purposes, are not as yet substances which it is the duty of the public analyst to examine in his official capacity, not being included under any of the designations food, drink, or drugs. It is our opinion that considerable advantage to the public at large would result were the scope of the Food and Drugs Acts considerably augmented, so that the public analyst should officially examine many substances in every-day use other than merely edible or potable matters.

Soaps generally may be classified into four groups, viz.:

(1) Scouring soaps and analogous substances used by manufacturers.

(2) Household or laundry soaps.

(3) Medicated soaps.

(4) 'Fancy' soaps.

Of the first group, nothing need be said in reference to

the necessity of analysis; those consumers who require such quantities of materials as to make their orders of a wholesale nature have it well within their power to protect themselves against possible fraud by simply contracting for goods of specified quality, and employing the services of a competent analyst to ensure that they are actually supplied with products of the required nature.

Soaps of the second class are ordinarily retailed to the general public by grocers and others; very great divergencies exist between the intrinsic qualities of soaps sold in this way for household purposes, and these differences are by no means always taken into account in the price. Of course it cannot be expected that a soap sold at 3d. per lb. should be identical in quality with one sold at 4d. per lb.; but it is evident that the cheaper article ought to contain at any rate three-quarters of the amount of actual soap (apart from water, etc.) that is present in the dearer one, and more still if the soap itself is made from cheaper materials (coarser fatty matters) in the first instance. It would seem that no injury would result to the trade of the honest dealer if certain standards of quality as regards percentage of actual soap were adopted, so that any article sold as soap of such and such a kind should of necessity contain not less than such and such a percentage of actual soap (*e.g.*, a curd soap of first quality might be required to contain not less than 70 per cent. of actual soap, and so on for other qualities). If the public really requires and will have an inferior article, 'let down' with water and 'closed up' by addition of saline matters, such products should be sold with a notification to the purchaser that they are not genuine soaps. In the same kind of way, soaps treated with silicate of soda for the purpose of increasing detergence and diminishing cost of production, through incorporation of large amounts of water, should be sold as 'silicated soaps,' and not under names calculated to give the impression that they are true soaps devoid of admixture.

As regards medicated soaps, this is not the occasion to discuss the question as to whether such articles should or should not be regarded as patent medicines subject to stamp duty; but it is obvious that if an article is sold on the understanding that it contains a certain medicinal agent incorporated therewith, the which agent is not there,

or, if present, is contained to a materially smaller extent than is represented, the purchaser is much wronged. It might, perhaps, be difficult to fix standards for such a substance as carbolic acid soap ; but it does not seem impracticable, even in such a case as this, to insist on a given minimum of carbolic acid, etc., being present in an article sold under such a name. It is by no means infrequent to find soaps sold, for application to the skin more especially, as containing sulphur, glycerine, honey, milk, cream, etc., and represented as being for that reason highly beneficial, when in point of fact no trace of any such constituent is actually present.

The fourth class of soap above referred to is almost invariably sold in tablet form for convenience of use. Although the title 'toilet soap' or 'fancy soap' does not actually imply that the products, or the materials from which they are made, have been specially refined and purified so as to render the soap innocuous to tender and sensitive skins, yet there is a general impression that such is the case, and that in consequence such tablets are worth several times as much as domestic soaps ; in fact, it is only in virtue of this implied understanding that the public pays the enhanced prices usually charged for this class of article. The actual state of the case, however, is very far from being in accordance with this fact.

The soaps of commerce may be divided broadly into 'hard' and 'soft' soaps. The hard soaps are made of the various animal and vegetable oils and fats saponified with caustic soda ; the soft soaps are manufactured from the fish and other low-grade oils, potash being used in the saponification.

100 parts of neutral glyceride produce about 150 parts of finished soda soap.

Resin is a legitimate substitute for fatty matter in the common soap, as used for household and manufacturing purposes, as the resinates possess powerful detergent properties.

Soap-powders, washing-powders, dry soaps, etc., are generally mixtures of carbonate of soda with dried and powdered soap, sometimes with the addition of soda sulphate and other inert materials.

The Analysis of Soap.

Water.—10 grammes of a representative sample is weighed out after being reduced to the state of thin slices or shavings. It is dried at 50° C., which is afterwards raised to 105° C., and continued at this temperature till no further loss of weight is noted. The object of drying at the lower temperature is to prevent the soap melting, and thus making it very difficult to dry to constant weight.

In the best curd soaps the water varies from 12 to 20 per cent., whereas in some common soaps, such as those made from palm oil, the water may reach 75 per cent.

Uncombined Fat.—The residue, after drying, is exhausted with petroleum ether. This will dissolve out any unsaponified fatty matter—hydro-carbon oils (unsaponifiable matter), phenols, cresols, etc., that may be present in the soap. The petroleum ether is separated, distilled off, and the residue weighed.

Total Alkali.—The residue after treatment with petroleum ether constitutes the soap proper, and any mineral additions that may be present. This is treated with about 200 cc. of hot alcohol until all that will is dissolved. The alcoholic solution is then filtered, and the filter washed with alcohol. The filtrate is then made up to a definite volume, and divided into two parts—*a* and *b*.

(*a*) To this solution (= 5 grammes of the original sample) are added one or two drops of solution of phenol-phthalein, and the liquid titrated with $\frac{N}{10}$ HCl until the pink colour is just discharged. The alkalinity found is calculated to NaHO as *free alkali*.

(*b*) The second portion of alcoholic solution (= 5 grammes original soap) is diluted with water, two or three drops of solution of methyl-orange added, and the solution titrated with $\frac{N}{2}$ HCl. This will equal *total alkali*, which is calculated to K_2O or Na_2O as the case may be.

The residue, if any, left on the filter after treatment with alcohol may consist of carbonate, silicate, or borate of the alkalies ; other substances, such as starch, sand, clay, etc., added as ' fillers ;' pigments, as ultramarine, umber, ochre.

The residue is treated with water, and filtered. Starch, clay, sand, etc., will remain undissolved. This residue

is further examined if necessary. This solution, after making up to a definite volume, is tested for carbonates, borates, and silicates. Half the solution should be evaporated in a platinum dish with hydrochloric acid twice to complete dryness, taken up in water, and the residual silica filtered off, washed, and weighed. The silica so found is calculated to silicate of sodium.

Carbonates or borates, if present, may be titrated with standard acid.

Fatty and Resin Acids.—5 grammes of the soap is dissolved in hot water (cooled and exhausted with ether if free glycerides or unsaponifiable matter is present), and then decomposed with a slight excess of dilute sulphuric acid. The precipitated acids are then taken up in ether, the ethereal solution washed free from acid with water; the ether distilled off, and the residue dried to constant weight.

The residue will be fatty acids, and, if present, resin acids.

Resin.—The resin is estimated in the fatty acids by the method devised by Gladding. About 0·5 gramme of the mixture of the fatty acids and resin is dissolved in 20 cc. of strong alcohol, and with phenol-phthalein as indicator $\frac{N}{10}$ NaHO is run in until there is a slight excess. The alcoholic solution, after boiling for ten minutes to ensure complete saponification, is mixed with ether in a graduated cylinder till the volume is 100 cc. To the alcoholic and ethereal solution 1 gramme of very finely-powdered silver nitrate is added, and the contents of the cylinder are shaken thoroughly for ten or fifteen minutes. After the precipitate has settled, 50 cc. are measured off, and, if necessary, filtered into a second graduated cylinder. A little $AgNO_3$ is added to see if the precipitation is complete, and then 20 cc. of dilute hydrochloric acid (1 to 2) is added to decompose the silver resinate. An aliquot part of the ethereal solution in the cylinder is evaporated in a tared dish and weighed as resin, deducting a small correction for oleic acid (for 10 cc. deduct 0·00235 gramme). The amount of resin so found, subtracted from the combined fatty acids and resin as found before, gives the amount of fatty acids.

Estimation of Carbolic Acid.—J. Lewkowitsch has found the following method sufficiently accurate for all

practical purposes : 50 grammes of the sample is dissolved in water, and about 20 cc. of 10 per cent. potash added to combine with the free phenols and cresols present. The solution is then treated with a large excess of strong brine. This will precipitate the soap as a granular mass. The supernatant liquid is then separated, and the soap again washed with a further quantity of brine, which is again repeated if necessary. The solution of the phenates and cresolates is evaporated to small bulk, and then introduced into a graduated tube (or, better, a Muter's carbolimeter). Add more salt if necessary, then acidify with hydrochloric acid ; the volume of the separated phenols and cresols is read off and taken as so many grammes.

Analyses of some Soaps of Commerce.

	Curd.	Curd.	Castile.	Castile (Mottled).	Tallow.	Tallow.	Soft.
Water	28·1	27·0	14·0	22·2	20·9	35·0	38·4
Fatty acids ...	67·4	68·0	77·0	67·7	71·0	45·0	48·4
Combined alkali	7·5	7·7	8·7	9·0	8·9	6·0	12·0
Free alkali ...	·1	·2	·3	·4	·3	2·1	3·2
Silica	·3	·8	none	·2	none	7·0	·2
Insoluble in alcohol			1·1	2·1	1·6	7·7	1·1
Total	103·4	103·7	101·1	101·6	102·7	102·8	103·3

THE ASSAY OF QUININE AND ITS PREPARATIONS.

Testing the Purity of Quinine Sulphate. (*Official Directions.*)* *Test for Cinchonidine and Cinchonine.* —Heat 10 grammes of the sulphate of quinine in 250 cc. of boiling water, with 3 or 4 drops of dilute sulphuric

* The decimal equivalents of the grain weights are given for convenience of working.

acid. Set the solution aside until cold. Separate, by filtration, the purified sulphate of quinine which has crystallized out. To the filtrate, which should nearly fill a flask, add ether, shaking occasionally, until a distinct layer of ether remains undissolved. Add ammonia in very slight excess, and shake thoroughly, so that the quinine at first precipitated shall be redissolved. Set aside for some hours, or during a night. Remove the supernatant clear ethereal fluid, which should occupy the neck of the vessel, by a pipette. Wash the residual aqueous fluid and any separated crystals of alkaloid with a very little more ether, once or twice. Collect the separated alkaloid on a tared filter, wash it with a little ether, dry at 100° C., and weigh. Four parts of such alkaloid correspond to five parts of crystallized sulphate of cinchonidine or of sulphate of cinchonine.

Test for Quinidine.—Recrystallize 5 grammes of the original sulphate of quinine, as described in the previous paragraph. To the filtrate add solution of iodide of potassium, and a little alcohol to prevent the precipitation of amorphous hydriodates. Collect any separated hydriodate of quinidine, wash with a little water, dry, and weigh. The weight represents about an equal weight of crystallized sulphate of quinidine.

Test for Cupreine.—Shake the recrystallized sulphate of quinine, obtained in testing the original sulphate of quinine for cinchonidine and cinchonine, with 44 cc. of ether and 10 cc. of solution of ammonia, and to this ethereal solution, separated, add the ethereal fluid and washings also obtained in testing the original sulphate for the two alkaloids just mentioned. Shake this ethereal liquor with 10 cc. of a 10 per cent. solution of caustic soda, adding water if any solid matter separates. Remove the ethereal solution. Wash the aqueous solution with more ether, and remove the ethereal washings. Add diluted sulphuric acid to the aqueous fluid heated to boiling, until the soda is exactly neutralized. When cold, collect any cupreine sulphate that has crystallized out on a tared filter, dry, and weigh.

Quinine sulphate should not contain more than 5 per cent. of other cinchona alkaloids. The British Pharmacopœia gives the formula of crystallized quinine sulphate as $[(C_{20}H_{24}N_2O_2)_2H_2SO_4]_2 15H_2O$. The freshly-prepared salt is stated to lose 15·2 per cent. water at 100° C.

Estimation of the Alkaloidal Strength of 'Scale Preparations.—Dissolve 5 grammes in 30 cc. of water, place the solution in a separator, add 20 cc. of chloroform, and then a slight excess of ammonium hydrate. Shake well and allow it to stand. When the chloroform has separated off clear, run it off into a small weighed basin, and repeat the shaking successively with two portions of 10 cc. and one of 5 cc. of chloroform, always running it off into the same basin. Evaporate off the chloroform on the water-bath, and dry the residue for half an hour in the air-bath at 100° C., and weigh. Thus treated, citrate of iron and quinine should show 15 per cent. of alkaloidal residue, which should be soluble in ether.

This is the process contemplated by the British Pharmacopœia, but the American method of taking 4 grammes in 30 cc. water, adding ·5 gramme of tartaric acid, then a decided excess of solution of soda, and finally shaking out with four successive portions of chloroform of 15 cc. each, gives less trouble in practice, as the chloroform does not emulsify so badly. The use of the air-bath gives really anhydrous quinine, but, for ordinary purposes, drying to constant weight in the water-oven will do.

Estimation of Total Alkaloid in Tincture of Quinine.—This is determined by the process given under 'Tincture of Nux Vomica.'

Assay of Cinchona Bark.—Process of the British Pharmacopœia for ascertaining the amount of (1) quinine with cinchonidine, and (2) total alkaloids, in the succirubra or red cinchona bark (Cinchonæ Rubræ Cortex, British Pharmacopœia):

1. *For Quinine and Cinchonidine.*—Mix 20 grammes of the bark in No. 60 powder with 6 grammes of calcium hydrate; slightly moisten the powder with 25 cc. of water; mix the whole intimately in a small mortar or dish; allow the mixture to stand for an hour or two, when it will present the characters of a moist, dark-brown powder, in which there should be no lumps or visible white particles. Transfer this powder to a 6-oz. flask, add 130 cc. of a mixture of 3 volumes of commercial benzol and 1 volume of amylic alcohol (Benzolated Amylic Alcohol, British Pharmacopœia); boil them together for half an hour; decant, and drain off the liquid on to a filter, leaving the powder in the flask; add more of the benzol liquid to the powder, and boil and decant as before; repeat this opera-

tion a third time ; then turn the contents of the flask on to a filter, and wash by percolation with more of the liquid until the bark is exhausted. The flask during the above boilings is best fitted to an inverted condenser. Introduce the collected filtrate while still warm into a glass separator ; add to it 2 cc. of dilute hydrochloric acid, mixed with 10 cc. of water ; shake them well together, and when the acid liquid has separated this may be drawn off, and the process repeated with distilled water slightly acidulated with hydrochloric acid, until all the alkaloids are removed. The acid liquid thus obtained will contain the alkaloids as hydrochlorates, with excess of hydrochloric acid. It is then to be carefully and exactly neutralized with ammonia, and then concentrated to about 18 cc. If now 1·5 grammes of tartarated soda, dissolved in twice its weight of water, be added to the neutral hydrochlorates, and the mixture stirred with a rod, the insoluble tartrates of quinine and cinchonidine will separate in about an hour ; and these collected on a filter, washed, and dried, will contain eight-tenths of their weight of the alkaloids, quinine and cinchonidine, which multiplied by 5 represents the percentage of these alkaloids. The other alkaloids will be left in the mother-liquor.

2. *For Total Alkaloids.*—To the mother-liquor from the preceding process add ammonia in slight excess. Collect, wash, and dry the precipitate, which will contain the other alkaloids. The weight of this precipitate multiplied by 5, and added to the weight of the quinine and cinchonidine, gives the percentage of total alkaloids.

De Vrij's Method for Separation of the Mixed Alkaloids from Cinchona Barks.—Twenty grammes of the finely-powdered bark is treated with 5 grammes of strong hydrochloric acid, mixed with 20 cc. of water, and the resulting paste allowed to stand for some hours. More water is then added, until the whole is sufficiently fluid to pour freely. The mixture is now transferred to a percolating tube plugged with threads of old linen.* The percolate is returned to the tube until the fluid passes perfectly clear. Water is now supplied to the percolater until a little of the percolate ceases to give a precipitate on addition of excess of caustic soda, the tested portions being afterwards added to the percolate. The quantity of percolate which it is necessary to pass through the marc is usually from 180 cc.

* The material known in France as 'charpie.'

to 200 cc., which quantity will rarely be exceeded if the percolation has been successfully conducted. The estimation of the amount of alkaloids in this acid solution may be made in either of the following ways, viz. :

1. The acid solution is precipitated by a *large excess* of caustic soda, which throws down a curd-like *white* precipitate. The precipitate is collected on a double filter,* and washed until the filtrate is nearly colourless. The whole of the filtrate is measured, and compensation made by adding to the weight of alkaloid, to be presently ascertained, 0·0585 gramme for every 100 cc. of the mother-liquor at temperature 15° C. The drained filter is carefully dried upon blotting-paper until the precipitate ceases to adhere, when it may be easily detached without loss, and transferred to a small tared dish. It is now dried over a water-bath until it ceases to lose weight, and the weight is ascertained. Add the compensation above indicated for mother-liquor, multiply the sum by five, and the product is the percentage of alkaloids in the bark under examination.

The alkaline mother-liquor may now be used for ascertaining indirectly the percentage of cincho-tannic acid. After exposure for two or three days in a shallow dish, by which the cincho-tannic acid becomes converted into cinchona red,† the liquid is heated, and hydrochloric acid cautiously added to slight acid reaction. After cooling, the now turbid liquor is filtered through a double filter to collect the very voluminous precipitate of cinchona red. The precipitate is washed, dried, and weighed, the second filter being used as a tare.‡ By multiplying the ascertained weight of cinchona red by 1·2, a close approximation to the weight of cincho-tannic acid is obtained, from which its percentage may be calculated, and it will be seen that the quantity of cincho-tannic acid in different species of cinchona, and even in different samples of the same species, varies considerably.

* Doubling the filter facilitates the filtration.

† If the dark-red alkaline liquor becomes turbid during exposure to air, the quantity of caustic soda is insufficient for solution of the newly-formed cinchona red, and more soda must be added.

‡ Although De Vrij is opposed to drying precipitates upon the filter, it is unavoidable in this case, because the moist cinchona red cannot be conveniently removed.

2. The acid solution is mixed with excess of caustic soda as before, and well shaken in a bottle with 1 litre of commercial benzol, and left standing for not more than five minutes, for the benzol, which now contains the alkaloids in solution, to separate.* The benzol solution is now decanted on a filter previously moistened with benzol, and the remainder is poured into a separating funnel. After sufficient time for separation, the red alkaline liquor is drawn off into the bottle previously used, and shaken with other 200 cc. benzol to remove possible traces of alkaloid, and this benzolic solution is also filtered and added to the former. The amount of alkaloids contained in the mixed benzolic solutions may now be determined either directly or indirectly in the manner following, viz. :

Direct Determination.—The benzolic solution is shaken with 30 cc. very dilute nitric acid, the acid solution is drawn off and replaced by 20 cc. water, which is again shaken and added to the first. The liquors are heated to drive off traces of benzol, and when cool transferred to a separator and shaken with 200 cc. ether, and an excess of caustic soda. In this way *all* the alkaloids are dissolved by the ether,† leaving generally a slight brown film on the surface of the alkaline liquor, *which is almost entirely soluble in chloroform.*‡ After separating the ethereal solution a further 100 cc. ether is shaken with the alkaline liquor, and is then added to the first. By distillation of the ether, the whole of the alkaloids are left in a state of

* A litre of benzol (boiling at from 85° to 120° C.) dissolves all the alkaloids of 20 grammes of bark. By long standing, however, a slight separation of crystallized benzolate of alkaloid, chiefly cinchonine, may sometimes take place and affect the accuracy of the result. De Vrij, therefore, recommends that it should not be allowed to stand for more than five minutes. The benzol may be used repeatedly, without redistillation, and with but little loss.

† De Vrij found that the succirubra bark used in Bengal for the manufacture of cinchona febrifuge proved an exception to this rule; for, although the whole of the alkaloids are at first dissolved by the ether, a separation of small crystals of cinchonine quickly followed to the extent of 0·17 gramme. De Vrij attributes this to the large proportion of cinchonine contained in this bark, which he has found to amount to as much as 49·3 per cent. of the total alkaloids.

‡ This brown substance, *which is not alkaloid*, is the reason why analyses of bark, in which chloroform is the solvent, yield an apparent higher percentage of alkaloids.

greater purity than I have ever obtained them by any other process.

Indirect Determination.—The benzolic solution is well shaken with 70 cc. decinormal sulphuric acid. The acid solution is drawn off and replaced by 30 cc. water, which is again shaken and added to the other. The aqueous liquors are heated, and *accurately* neutralized by decinormal solution of caustic soda until the colour of reddened litmus is affected by it. The quantity of soda solution required for saturation is now to be deducted from 70 cc. (the equivalent of 70 cc. decinormal sulphuric acid), and the difference multiplied by ·031* is the weight of alkaloid in 20 grammes of bark. This product multiplied by 5 gives the percentage.

Example.—Suppose the bark for analysis to contain 5 per cent. alkaloid—which would be a reasonable standard for pharmaceutical purposes—the acid solution from 20 grammes powder should be neutralized by, say, 37·5 cc. soda solution :

For $$70 - 37{\cdot}5 \times {\cdot}031 \times 5 = 5{\cdot}04$$

(the number of grammes of alkaloid in 100 grammes of bark).

THE ASSAY OF OPIUM AND ITS PREPARATIONS.

Opium is the dried juice from the unripe capsules of the poppy (*Papaver somniferum*). Opium is produced in European and Asiatic Turkey, India, Persia, China, etc. Opium varies very much in appearance, composition, and quality, according to its origin and mode of preparation. Smyrna opium is described as follows in the British Pharmacopœia (1885) : 'In rounded, irregularly formed masses, varying in weight, but commonly about 8 oz. to 2 lb., usually covered with portions of poppy leaves, and scattered over with the reddish-brown chaffy fruits of a species of rumex. When fresh, plastic, and internally moist, coarsely granular, and reddish or chestnut-brown, but becoming harder by keeping, and darkening to

* 0·031 gramme is the weight of alkaloid corresponding to 1 cc. of a decinormal solution, the molecular weight of the mixed alkaloids of cinchona bark being, as previously stated, 310.

blackish-brown. Odour strong, peculiar, narcotic; taste nauseously bitter.'

The composition of opium is very complex. It consists of gummy matter to the extent of about 50 per cent.; water from 8 to 30 per cent.; ash 4 to 8 per cent.; morphine 7 to 16 per cent.; narcotine 4 to 8 per cent., with small quantities of resinous and other matters.

Opium is occasionally adulterated, the following substances being mentioned as adulterants by various writers: Gum arabic, gum tragacanth, starchy substances, and the pulp of apricots and figs; also various make-weights, such as exhausted opium, together with excessive moisture. Tannin and starch are not present in pure opium.

The most important constituents of opium are the alkaloids, which are very numerous. The alkaloid morphine is of the greatest therapeutic importance. The percentage of morphine varies very much in various samples of opium. Smyrna opium frequently contains from 12 to 15 per cent., whereas East India opium contains much less. The best commercial opiums yield about 18 per cent. of morphine reckoned on the powdered drug. The morphine exists in opium in combination with meconic acid. Meconic acid derives its chief analytical interest from the fact that it is strictly peculiar to opium, and hence its positive detection is a proof of the presence of a preparation of opium. Opium contains on the average about 4 per cent. of meconic acid combined as meconate of morphine, which is soluble in water. On the addition of a neutral solution of Fe_2Cl_6 to meconic acid or a meconate, a characteristic deep purplish-red colouration is produced.

Morphine crystallizes, when perfectly pure, in white or colourless prismatic forms, or as a crystalline powder, having the composition $C_{17}H_{19}NO_3+H_2O$. The crystals may be dried at temperatures not exceeding 100° C. (212° Fahr.), without decomposition. In the usual methods of analysis morphine is obtained in the shape of minute crystals, always coloured more or less deeply yellowish-brown or buff-coloured, by extractive matter that remains in them. If sufficiently pure these crystals will dissolve, in 100 times their weight of lime-water, to a clear solution, leaving no appreciable residue. The morphine in opium can be dissolved out by the action of lime-water, and from this solution it is precipitated by the action of ammonium chloride or ammonia in slight excess.

Morphine readily dissolves in solutions of the fixed alkalies and of the alkaline earths, but only sparingly in ammonia.

A useful solvent for morphine is a mixture of equal volumes of ether and ethyl acetate; but even in this its solubility is limited, especially in the crystallized state.

Amylic alcohol dissolves morphine sparingly in the cold (1 in 150), but when heated is a fairly good solvent (1 in 50). The alkaloid dissolves best when liberated from its salts in presence of amylic alcohol.

Cold water dissolves only about $\frac{1}{1000}$th of its weight of morphine; hot alcohol about $\frac{1}{30}$th; cold alcohol about $\frac{1}{90}$th. Morphine in the crystalline state is nearly insoluble in ether; when first liberated by the action of ammonia it dissolves more freely in ether, but soon separates again in the crystalline condition.

The salts of morphine, with the commoner acids and those present in opium, are soluble in water, so that water will extract all of the morphine from opium, at least after proper preparation.

From aqueous extracts of opium, ammonia precipitates narcotine and certain organic matters, both being redissolved by ether.

Narcotine is insoluble in water, but owing to the feebly acid reaction of aqueous extracts of opium, the narcotine also dissolves, combined with various acids present. If ammonia is added to the solution, together with ether, the narcotine at first precipitated is redissolved by the ether and remains in solution, even after standing a long time.

Assay of Opium.—The assay of opium for morphine has received very much attention at the hands of various chemists. Many of the processes are both tedious and complex, so for the purposes of this small work we will only give the official process.

The British Pharmacopœia process, devised by M. Conroy, is very simple and rapid, and in careful hands gives very fair results. This method is based on the conversion of the resinous matters of the opium into insoluble lime compounds; the decomposition of the morphine meconate with the formation of insoluble calcium meconate; the solubility of the free morphine produced in lime-water; the decomposition of the solution by ammonium chloride, with formation of calcium chloride, ammonia and free morphine; the use of alcohol to dissolve impurities, and

of ether to promote the crystallization of the alkaloid; and the collection and washing of the morphine so obtained. The process is carried out as follows: 7 grammes* of the opium dried at 212° Fahr. (100° C.), and 3 grammes of freshly slaked lime are triturated together with 20 cc. of distilled water in a mortar until a uniform paste is produced, then add 50 cc. of distilled water and stir occasionally during half an hour. Filter the mixture through a plaited filter about 3 inches in diameter into a bottle or flask (having a capacity of about 6 oz.) marked at exactly 52 cc., until the filtrate reaches the mark. To the filtered liquid (representing 5 grammes of the opium) add 5·5 cc. of alcohol (of about ·838 specific gravity) and 25 cc. of ether, shake the mixture and add 2 grammes of ammonium chloride, shake well and frequently during half an hour, then set aside for twelve hours.† Counterbalance two small filter-papers: place one within the other in a small funnel, and decant the ethereal layer as completely as practicable upon the inner filter. Add 10 cc. of ether to the contents of the flask, and rotate it; again decant the ethereal layer upon the filter, and afterwards wash the latter with 5 cc. of ether added slowly and in portions. Now let the filter dry in the air, and pour upon it the liquid in the flask in such a way as to transfer the greater portion of the crystals to the filter. When the liquid has passed through the filter wash the flask, and transfer the remaining crystals to the filter with several small portions of distilled water, using not more than 10 cc. in all, and distribute the portions evenly upon the filter. Allow the filter to drain, and dry it, first by pressing between filter paper, and afterwards at a temperature of between 55° and 60° C., and finally at from 90° to 100° C. until constant in weight. Weigh the crystals in the inner filter, counterbalancing by the outer filter. The crystals should weigh 0·5 grammes, or not less then 0·475 grammes, or more than 0·525 grammes, corre-

* For convenience we have converted the grain weights directed to be used in the Pharmacopæia to their decimal equivalents.

† As suggested by Conroy, and proved by Braithwaite and Farr, the time allowed for precipitation of the morphine may be reduced from twelve hours to two without affecting the accuracy of the results, but it is safer to allow six or eight hours to elapse before filtering.

sponding to about 10 per cent. of morphine. This standard is ridiculously low, and necessitates the diluting of commercial opium with exhausted marc to bring the percentage of alkaloid down to the pharmacopœial amount, or the substitution of a proportionally smaller quantity of the drug when used for the manufacture of the various preparations of opium. 'It is all very well to standardize, but I think it is going too far when we attempt it with natural products; but if we are to have a maximum and minimum standard for opium, let it be one which will exclude the inferior and adulterated kinds, instead of the reverse as now obtains. To attain this it would be necessary to raise the standard at least 2 per cent.' (M. Conroy, *Pharmaceutical Journal* (3), xvi. 378).

The pharmacopœial process for the assay of opium yields results rather below the truth, but it is the best published process for ordinary commercial work.

Extract of Opium (B.P.) is made by exhausting the opium with cold water, straining and evaporating the liquid to half the weight of the opium used. It has a pilular consistency, and should yield on assay by the Pharmacopœia process about 20 per cent. of morphine. It is best to employ 3·5 grammes of the extract instead of the 7 grammes as directed under opium, multiplying the weight of crystals obtained by forty instead of twenty, as the morphine obtained is from 2·5 grammes of the extract.

Liquid Extract of Opium (B.P.) is prepared by macerating 1 oz. of the solid extract with 16 oz. of water, adding 4 oz. of rectified spirit, and filtering. It should contain '22 grains of the solid extract in nearly 1 fluid oz.' The specific gravity should be between ·985 and ·995, and when assayed by the process prescribed for opium 'should yield about 1 per cent. of morphine.'

Tincture of Opium (B.P.).—For the making of this important preparation the Pharmacopœia directs as follows: Macerate $1\frac{1}{2}$ oz. of opium in powder in 1 pint of proof spirit for seven days in a closed vessel with occasional agitation, then strain, press, filter, and add sufficient proof spirit to make 1 pint. It contains the soluble matter of 33 grains of opium in 1 fluid oz., or about 0·75 per cent. morphine as bimeconate of morphine, together with the other opium alkaloids. No specific gravity or mode of

testing this preparation is given in the Pharmacopœia, but it is evident that the process as given under opium may be applied after evaporating off the alcohol.

The Alcoholic Strength is determined by direct distillation. It is best to dilute 50 cc. of the tincture to 100 cc. with water ; about 95 cc. is distilled off. This is made up to 100 cc. at 15·5° C. The specific gravity is taken, and the alcoholic strength is found by reference to the alcohol tables, multiplying the result, of course, by two. A piece of platinum wire or pumice-stone placed in the flask will prevent bumping.

We have examined forty-five samples of tincture of opium made strictly according to the British Pharmacopœia process, with the following results :

Specific gravity at 15·5° C.	·930 to ·941.
Alcoholic strength	3·0° to 7·0° under proof.
Total solids	3·0 to 5·1 per cent.

The **Morphine** is determined by the British Pharmacopœia process. The alcohol is first boiled off by evaporating on a water-bath ; the lime is then added into the residue, and the mixture rubbed down with the water as directed under opium. It is useless to attempt the determination of the morphine by this process on a less quantity of the tincture than 50 cc. It is best to employ double this quantity if possible. S. J. Hinsdale (*Chemical News*, lxii. 77) has described a simple method of determining the morphine in tincture of opium by observing the depth of the blue or green colour produced on treating the sample with a freshly prepared mixture of ferric chloride and potassium ferricyanide solutions.

COMPOUND TINCTURE OF CAMPHOR.

This important preparation is generally known to the public as 'paregoric,' or 'paregoric elixir.' Compound tincture of camphor is direced to be prepared by the Pharmacopœia as follows : 40 grains each of opium and benzoic acid, 30 grains of camphor, and 30 minims of oil of anise, the whole being diluted to one pint.

Much of the paregoric of commerce is deficient in one or more of the above constituents. The alcohol being the

most expensive ingredient, there is a strong inducement to reduce its amount. The opium is the most important constituent; this is apt to be deficient in amount or wholly absent. This is due to the fact that paregoric cannot be legally sold except by registered pharmacists, hence a preparation called 'paregoric' destitute of opium is frequently sold by grocers and others.

The Specific Gravity should not much exceed ·927. The following are the results of the examination of fifty samples of genuine compound tincture of camphor:

Specific gravity at 15·5° C.	·922 to ·927.
Alcoholic strength	1 to 2·5 degrees under proof.

Alcoholic Strength.—This is determined as follows: 50 cc. of the sample is taken, and made up to 350 cc. by the addition of water. This causes a precipitation of the oil and resinous matter. The liquid is then clarified by adding a few drops of a strong solution of calcium chloride, followed by some sodium phosphate. The resultant precipitate of calcium phosphate entangles the oily and resinous matter. The liquid is now made up to 400 cc. with water, filtered through a dry filter, and 250 cc. of the filtrate distilled until about 200 cc. have passed over. The distillate is then made up to 250 cc., and the specific gravity taken at 15·5° C. If the foregoing instructions be adhered to, the percentage of 'proof spirit' corresponding to the specific gravity of the distillate, multiplied by eight, will be the percentage by volume contained in the tincture.

Opium.—The proportion of opium present can be approximately judged by the depth of the red colour produced, when the sample previously diluted with water or proof spirit is treated with a solution of ferric chloride. By comparing the tint obtained with that given by a sample of known quality, a fair criterion of the proportion of opium may be obtained.

Benzoic Acid.—25 cc. of the tincture is rendered alkaline with sodium hydrate, and evaporated to 10 cc.; a portion of the camphor and oil of anise will be volatilized. The liquid is then diluted slightly, and extracted with ether. This will remove the camphor and oil remaining from the liquid. The ether is separated, and the aqueous

liquid rendered acid with hydrochloric acid ; the free benzoic acid is then removed by agitation with ether. On allowing the separated ethereal solution to evaporate spontaneously in a small beaker, the benzoic acid is obtained in a fit condition for weighing.

An approximate determination of the benzoic acid may be made by determining the acidity of the tincture by titration with $\frac{N}{20}$NaHO, using phenol-pthalein as indicator. 10 cc. of the tincture is a convenient quantity of the tincture to titrate. Each cc. of the soda required = 0·0061 benzoic acid.

Methylic Alcohol.—Methylated spirit is sometimes used, wholly or in part, for the preparation of compound tincture of camphor and other tinctures. This sophistication is best detected by the Riche and Bardy test, which is performed as follows : Mix together in a flask 10 cc. of the sample, 15 grammes of iodine, and 2 grammes of amorphous phosphorus, and distil off the methyl and ethyl iodides formed into 30 cc. of water. Separate the heavy oily drops from the water, and mix with 5 cc. of aniline in a flask kept cool ; after an hour add some water, and an excess of soda solution, and boil. An oily layer rises to the top, and 1 cc. of this is mixed with 10 grammes of a mixture of 100 parts of clean sand, 2 of common salt, and 3 of cupric nitrate ; place the mixture in a glass tube, and heat for eight hours at a temperature of 90° C. ; then exhaust with warm alcohol, filter, and make up to 100 cc. with alcohol. If the sample is pure, the alcoholic liquid is red ; but if as little as 1 per cent. of methyl alcohol is present, the liquid has a distinct violet colour (due to methyl aniline violet), which is deeper according as the percentage of methyl increases. The presence of the aniline violet is corroborated by diluting a portion of the liquid with 2,000 times its volume of water, and immersing some white wool in it for half an hour. If the sample contained methylic alcohol, the wool takes on the violet colour, the depth of tint giving a fair approximate indication of the proportion of methylic alcohol present. In the case of methylic alcohol being found to be present, the skein of wool is compared with a standard set of skeins made from mixtures containing known percentages of methylic alcohol.

The above process, although reliable, is very tedious.

For qualitative examination, the following test, devised by Dr. Ashby, is both rapid and delicate: 10 cc. of a freshly-prepared 1 per cent. solution of sodium nitroprusside is mixed with an equal volume of the liquid to be tested, a few drops of ammonia added, and the colour of the solution examined after fifteen minutes. If a *red* colour develops, acetone or some of the other constituents of wood spirit is present.

To apply the above tests in the case of paregoric, the tincture is diluted and treated with calcium chloride and sodium phosphate, as in the estimation of the alcohol, and the first 10 or 20 cc. of the distillate tested by one of the above processes.

ASSAY OF NUX VOMICA PREPARATIONS.

Tincture of Nux Vomica.—The Pharmacopœia directs this important preparation to be made as follows: 133 grains of extract of nux vomica (containing 15 per cent. total alkaloids) is dissolved in a mixture of 16 oz. of rectified spirit, and 4 oz. of water. One fluid ounce of this tincture should contain 1 grain of total alkaloids.

An examination of twenty-four samples of commercial tincture of nux vomica, prepared as above, gave the following results:

Specific gravity at 15·5° C.	·892	to	·895
Alcoholic strength ...	21·0°	to	23·0° over-proof.
Total solids	0·9	to	1·1 per cent.

Total Alkaloids.—25 cc. of the tincture is evaporated nearly to dryness to drive off the alcohol; the residue is taken up in about 50 cc. of water, acidulated with sulphuric acid. The liquid is then transferred to a separator, and extracted with chloroform. This will extract the colouring matter, oil, resin, etc. The residue, after separating the chloroformic layer, is rendered faintly alkaline with ammonia, and again extracted with three successive treatments with chloroform. The chloroform containing the alkaloid is then washed once with water, filtered if necessary, and evaporated. The residue is then dried to constant weight. The B.P. tincture should contain 0·229 per cent. total

alkaloids, consisting of a mixture of strychnine and brucine.

Extract of Nux Vomica is prepared by exhausting the dried and powdered seeds with dilute spirit (4 : 1), and evaporating the filtered liquid until the residue on assay yields 15 per cent. of total alkaloids. The extract contains from 12 to 18 per cent. of water. For the estimation of total alkaloid, 1 gramme of the extract is dissolved in about 25 cc. of warm water, acidified, and treated as directed under the tincture.

TINCTURE OF RHUBARB.

Tincture of rhubarb is prepared by macerating 2 oz. of powdered rhubarb root, $\frac{1}{4}$ oz. each bruised cardamom seed and coriander fruit, $\frac{1}{4}$ oz. saffron in 1 pint of proof spirit.

This tincture as sold is frequently deficient in alcoholic strength and total solids; also the saffron ordered to be used in its preparation is not infrequently omitted.

The alcohol is determined by direct distillation, as given under tincture of opium. The alcoholic strength varies from 3 to 7 degrees under proof.

The total solids in genuine samples vary from 3 to 6 per cent.

Saffron is detected by the following test: Mix in a separator 5 cc. of the sample, 20 cc. of 2·5 per cent. KHO solution, and 10 cc. of ether; agitate well; separate the ethereal layer. Evaporate the ether, after filtering in a porcelain basin. Moisten the residue with concentrated sulphuric acid. A blue colour will appear if saffron is present.

AROMATIC SPIRIT OF AMMONIA.

Aromatic spirit of ammonia (*Spiritus ammoniæ aromaticus*) is the preparation popularly known as sal volatile. It is an alcoholic solution of about $1\frac{1}{4}$ per cent. of ammonia gas (NH_3), nearly $3\frac{1}{2}$ per cent. of neutral ammonium carbonate $(NH_4)_2CO_3$, and the volatile oils of lemon and nutmeg. Commercial samples of this preparation contain salts equivalent to from 1 to 3 per cent. of ammonia gas, the official spirit yielding a total of 2·5 per cent. of the gas.

Specific Gravity.—This varies from about ·896 to ·906.

Ammonium Carbonate.—This is best estimated by the nitrometer. About 10 cc. of the sample is introduced into the cup, and then allowed to run into the nitrometer, which is filled with mercury. This is followed by an excess of dilute hydrochloric acid. Carbon dioxide is then evolved by the action of the acid on the carbonate. The volume of gas is then noted and corrected to N.T.P., when each cc. of $CO_2 \times ·0042 =$ ammonium carbonate $(NH_4)_2CO_3$.

Aromatic spirits of ammonia should yield not less than seven times its volume of carbon dioxide.

Alcohol.—This is determined by direct distillation, after neutralizing with sulphuric acid. 50 cc. of the sample is rendered just acid, and made up to 100 cc. ; this is then distilled in the usual way.

The alcoholic strength varies from 10 to 18 degrees over-proof.

Total Alkalinity.—10 cc. of the spirit is diluted and titrated with $\frac{N}{2}$ HCl, using methyl-orange as indicator. Each cc. $\frac{N}{2}$ acid equals 0·3725 grain of NH_3 per fluid ounce, and 25·5 cc. should be required.

SPIRITS OF NITROUS ETHER.

Spirits of nitrous ether (*Spiritus æther nitrosi*) consists essentially of a solution of impure ethyl nitrite in alcohol. The Pharmacopœia assigns to this very important preparation the following characters : 'Transparent and nearly colourless, with a slight tinge of yellow, mobile, inflammable, of a peculiar penetrating apple-like odour, and sweetish cooling sharp taste. Specific gravity at 15·5° C., 0·840 to 0·845. It does not effervesce, or only feebly when shaken with a little sodium bicarbonate. When agitated in a test-tube with a strong solution of sulphate of iron, if a few drops of strong sulphuric acid are then poured down the sides of the tube, a deep olive-brown or black zone is produced, widening as the tube is gently shaken.'

The composition of spirit of nitrous ether varies very considerably, especially with regard to the amount of ethyl nitrite present. The tendency of this preparation to undergo gradual deterioration on keeping with the destruction of the nitrous ether is very great. It is established

beyond doubt that the presence of water hastens this decomposition ; hence the practice of adulterating this preparation with water, which is common, not only dilutes, but increases the tendency to decomposition.

Estimation of the Ethyl Nitrite.—The most ready method of determining this constituent is by means of the nitrometer. The application of this instrument to the assay of spirits of nitrous ether is due to A. H. Allen, and is recognised officially for the testing of this preparation.

Nitrites, when mixed with excess of potassium iodide and sulphuric acid, cause a liberation of iodine, and evolve all their nitrogen in the form of nitric oxide, according to the following equation :

$$C_2H_5.NO_2+KI+H_2SO_4=C_2H_5.HO+KHSO_4+I+NO.$$

The method of procedure is as follows : The nitrometer is first filled with brine. 5 cc. of the sample is placed in the cup, and, the control tube having been lowered, the spirit is allowed to enter through the tap, taking care that no air enters at the same time. 5 cc. of strong solution of potassium iodide is then allowed to enter, and after this 5 cc. of dilute sulphuric acid. Effervescence occurs, owing to the liberation of the gas ; the tube is well shaken, and the volume of gas, after standing ten minutes, observed. This is then corrected to the normal temperature and pressure by Charles's and Boyle's laws respectively, to calculate it from its volume in cc. to its weight in grammes, by multiplying the number of cc. of volume at N.T.P. by the weight of 1 cc. of the gas in grammes. This latter is easily obtained by multiplying the *crith* (·0896 grammes, weight of 1 litre of hydrogen) by the atomic weight of an elementary, or half the weight of a compound gas, and then dividing by 1,000. Suppose in the analysis 20 cc. of nitric oxide at 15° C. and 750 mm. barometer were obtained, and we require to know the weight of the gas at N.T.P. so that the amount of nitrite present can be calculated, then :

(*a*) $\frac{(273+0)\times 750\times 20}{(273+15)\times 760}=18{\cdot}79$ cc. corrected volume at N.T.P.

(*b*) $\frac{{\cdot}0896\times 15}{1000}={\cdot}001344$ grammes, weight of 1 cc. NO.

(*c*) $18{\cdot}79\times{\cdot}001344={\cdot}0253$ grammes of NO found

For official purposes, it is only necessary that spirits of nitrous ether should yield from seven to five times its volume of nitric oxide. If the gas were yielded from pure ethyl nitrite, this would be equivalent to 3 and 2 per cent. respectively. Even after keeping some considerable time, the preparation should not yield much less than five times its volume of gas.

Water.—This is estimated with sufficient accuracy by taking the specific gravity. The nitrous ether, though denser than alcohol, is present in too small a proportion to appreciably affect the results.

The specific gravity 0·845 (the B.P. standard) corresponds, according to the alcohol tables, to 81·7 per cent. absolute alcohol, or 152·4 per cent. proof spirit. The extent to which a sample has been diluted with water may be found by multiplying the percentage of proof spirit by the factor $0{\cdot}656 \left(=\frac{100}{152{\cdot}4}\right)$, when the product will be the percentage by volume of spirits of nitrous ether of B.P. specific gravity.

Methylic Alcohol.—Methylated spirit has occasionally been employed in the preparation of spirits of nitrous ether. For the detection of methylated spirit, the process due to J. T. Miller is the most satisfactory. About 30 cc. of the sample is shaken with 2 grammes of anhydrous carbonate of potassium, and, if needful, add fresh portions of the salt until it ceases to be dissolved ; then pour off the supernatant spirit. This serves to neutralize acid, and to remove water, of which an abnormal quantity may be present. Introduce about 15 cc. of the spirit into a small flask ; add 10 grammes of powdered anhydrous calcium chloride ; stir well together ; then, having connected the flask with a condenser, place it in a water bath, and distil until scarcely anything more comes over. The operation is rather slow, but needs little attention, and should be done thoroughly. The distillate contains nearly the whole of the nitrous ether and other interfering bodies, while in the flask there remains a non-volatile compound of calcium chloride and methylic alcohol if the latter is present. Now add to the contents of the flask 5 cc. of water, which decomposes the compound just referred to, and draw over the 5 cc. required for testing. Add it to an oxidizing

mixture of 2 grammes of potassium bichromate, 2 cc. of strong sulphuric acid, and 15 cc. of water; let the mixture stand for fifteen minutes, then distil 15 cc. Treat the distillate with a slight excess of carbonate of soda, boil rapidly down to 10 cc., and drop in cautiously enough acetic acid to impart a faint acid reaction; pour the liquid into a test-tube; add two drops of dilute acetic acid B.P., and 0·05 nitrate of silver dissolved in about 2·5 cc. water; apply heat, and boil for two minutes. If the spirit is free from methylic alcohol, the solution darkens, and often assumes transiently a purplish tinge, but continues quite translucent, and the test-tube, on rinsing out with water, appears clean, or nearly so. But if the spirit contains only 1 per cent. of methylic alcohol, the liquid turns first brown, then almost black and opaque, and a film of silver, which is brown by transmitted light, is deposited on the tube. When the sample is methylated to the extent of 3 or 4 per cent., the film of silver is sufficiently thick to form a brilliant mirror. This determination should be conducted in daylight.

ASSAY OF HYDROCYANIC ACID.

The dilute hydrocyanic acid of pharmacy is very liable to variation in strength.

The strength is determined by titration with $\frac{N}{10}$ $AgNO_3$. About 5 grammes of the sample is weighed out, diluted with water; a drop or two of litmus solution added; then caustic soda, until a strong alkalinity is produced. The silver solution is then carefully run in until a faint permanent cloud of silver cyanide is produced. The reaction is as follows:

$$(a)\quad \underbrace{2HCN}_{54}+2NaHO=\underbrace{2NaCN}_{98}+2H_2O.$$

$$(b)\quad \underbrace{2NaCN}_{98}+\underbrace{AgNO_3}_{170}=AgCN.NaCN+NaNO_3.$$

$\therefore$ 1000 cc. $\frac{N}{10}$ $AgNO_3$=5·4 grammes HCN.

Diluted hydrocyanic acid of the B.P. should contain 2 per cent. of real hydrocyanic acid (HCN).

URINE.

For the purposes of clinical diagnosis, it is absolutely essential to ascertain the total amount of urine voided during a period of twenty-four hours, especially in the case of morbid conditions, such as the presence of sugar, etc. The analysis of a urine is of very little use to the medical man unless it represents the composition of the urine passed during this period. A healthy human being of about 140 lb. weight excretes in twenty-four hours about 50 oz. of urine. This will have a specific gravity of about 1·020, and will contain about 4 per cent. of total solids, or nearly 20 grammes to the ounce.

The data usually required are the specific gravity, reaction to litmus, colour, the amount of urea, the presence or absence of albumen and glucose, and if present, the amount. The characters of the deposit, if any, should be very carefully noted, both chemically and microscopically. Uric acid and bile acids are also tested for, and in some cases it is desirable to know the amount of total solids, chlorides, sulphates, phosphates, etc.

Urine is of a pale yellow or reddish-yellow colour if normal. When blood is present, the urine has a brownish-red colour, and is often greenish or greenish-brown in tinge if bile acids are present.

Normal urine may be turbid, owing to the presence of urates, phosphates, or mucus. Urates will dissolve on warming with potash and phosphates on acidifying with acetic acid.

For general purposes, it is best to state the results of analysis in percentages, or better in grammes per 100 cc. in preference to grains per ounce or pint.

The **Specific Gravity** is taken at 15·5° by the bottle or Westphal balance. This ranges in healthy urine from 1·014 to 1·030. In diabetes the specific gravity occasionally reaches 1·062, whereas in albuminuria and diabetes insipidus it may fall as low as 1·005.

The **Reaction** to litmus is carefully ascertained by adding a few drops of litmus to a portion of the sample. Normal urine should be faintly acid. Healthy urine may, however, especially in warm weather, undergo an alkaline fermentation, caused by the micrococcus ureæ, which converts the urea present into ammonium carbonate.

Albumen may be tested for by the following tests :

Boiling Test.—The urine is rendered very faintly acid with acetic acid, and raised to the boiling point. Albumen, if present, precipitates in the form of a cloud or dense coagulum, dependent on the amount present.

Bodeker's Test.—To about 10 cc. of the urine faintly acidulated with acetic acid, a solution of ferro-cyanide of potassium is added drop by drop. If a precipitate forms, albumen is present.

Picric Acid Test.—An equal volume of clear saturated solution of picric acid is added to the urine. If a turbidity or precipitate forms, the tube is heated to boiling. If the precipitate is due to peptones or alkaloidal bodies, it will dissolve, while if the precipitate remains permanent, albumen is present.

Estimation of the Albumen.—An approximate estimation may be made by testing in an albuminometer. In this instrument the albumen is precipitated by various reagents, and the volume of the precipitate measured. There are many forms of this instrument—Esbach's is the best—but they are all very inaccurate. The albumen is best estimated gravimetrically by boiling a measured volume of the faintly acidified urine until all the albumen is coagulated. The flocks of albumen are then filtered off, well washed with water, and dried at 100° C.

Glucose may be tested for by the following tests :

Fehling's Test.—The urine is made alkaline with caustic potash ; any phosphates which may be deposited are filtered off. Fehling's copper solution* is then added to the

* Fehling's solution is best made as follows : 34·64 grammes of pure crystallised sulphate of copper is dissolved in distilled water and the solution diluted to 500 cc. 70 grammes of caustic soda and 180 grammes of recrystallised potassium sodium tartarate (Rochelle salt) are dissolved in about 400 cc. of water and the solution diluted to 500 cc. These two solutions are mixed in equal proportion just before use.

The following are the weights of the different sugars that will completely reduce 10 cc. of this solution :

10 cc. Fehling's solution	=	·0500	grammes	dextrine, lævulose or invert sugar.
10 cc. „	„	= ·0475	„	cane sugar (after inversion).
10 cc. „	„	= ·0678	„	lactose (milk sugar).
10 cc. „	„	= ·0807	„	maltose (malt sugar).

filtrate, which is then carefully raised to boiling. If cuprous oxide is precipitated, glucose is present.

Moore's Test.—The urine is slightly acidified with acetic acid, and boiled; albumen, if present, is removed by filtration. An excess of 10 per cent. caustic potash solution is then added, and the liquid boiled. Normal urine will yield a reddish-brown liquid; but if sugar is present, the liquid will become deep brown or black.

Nylander's Test.—1 cc. of the urine is added to 10 cc. of Nylander's reagent, and gently boiled; if even traces of sugar are present, the solution will become black. The reagent is made as follows: 2·5 grammes of pure bismuth oxynitrate (free from silver) and 4 grammes of Rochelle salt are dissolved in 100 cc. 8 per cent. solution of sodium hydrate.

Dr. Johnson's Test.—4 cc. of the urine is mixed with an equal volume of a saturated solution of picric acid in a test-tube; to this mixture is added 2 cc. of a 6 per cent. solution of caustic potash. An orange-red colour instantly appears as a result of the incipient reducing action of the kreatinine upon picric acid at ordinary temperatures. The colour is deepened by boiling, and if after the liquid has been kept at the boiling point for about a minute a bright red colour appears through the test-tube when held up to the light, the urine for clinical purposes may be confidently pronounced free from sugar. If an aqueous solution of glucose in the proportion of not more than 2 grains to the ounce be tested in the manner described, the liquid will be rendered so dark that no light is visible through the full diameter of the tube.

The Estimation of Sugar in Urine.—Sugar in urine is best determined by Dr. Pavy's modification of Fehling's process. Dr. Johnson's picric acid process, when applied quantitatively, is a very rapid method suitable for clinical purposes, and gives accurate results.

The Estimation of Sugar by Pavy's Method.—This method is a modification of Fehling's process, where instead of weighing the copper in the form of cuprous oxide, as in the ordinary method, the modification devised by Dr. Pavy depends on the fact that cuprous oxide dissolves in ammonia, forming a colourless liquid. When the saccharine liquid to be tested is run into the boiling Pavy solution, instead of a bulky red precipitate falling and

obscuring the end reaction, the liquid changes from blue to colourless.

The Pavy solution is most readily made as follows: To 120 cc. of the ordinary Fehling solution is added 300 cc. of ammonia (specific gravity ·880), and 400 cc. 12 per cent. caustic soda solution ; the mixed solutions are then made up to 1 litre. 100 cc. of this solution has the same oxidizing power on glucose as 10 cc. of the ordinary Fehling solution.

Pavy's solution possesses a different oxidizing power on maltose and lactose from that exerted by Fehling's solution. Its reaction on invert sugar under the above-named conditions is only five-sixths of that exerted by Fehling's test. Hence 120 cc. of the latter are employed in making the ammoniacal solution instead of 100, as would be the case if they were strictly equivalent (A. H. Allen).

The process is applied to the estimation of glucose in urine as follows : 10 grammes of the urine is diluted to 100 cc. with 10 per cent. ammonia solution. 20 cc. of the Pavy solution (=·010 grammes glucose) is diluted with 20 cc. of water, and placed in a flask of about 250 cc. capacity, which is fitted with an india-rubber stopper pierced with two holes. The flask is then fixed to the nozzle of a tapped burette, which is filled with the diluted ammoniacal urine. Through the second hole in the stopper is passed a short tube with a right angle bend, to which is attached a length of rubber tubing, which is used to convey the ammoniacal vapours given off during the titration out of a window.

The diluted Pavy solution in the flask is then gently boiled, and kept boiling during the titration with a low gas flame or spirit lamp. The saccharine liquid is allowed to run cautiously a little at a time into the flask until the blue colour is just discharged. Three titrations are made, and the mean result taken, when $\frac{100 \times \cdot 010}{\text{cc.'s used}} =$ per cent. of glucose in sample. Kreatinine, creatine, and traces of other substances normally present in urine, exercise a slight reducing action on Pavy's solution, though they do not interfere to so great an extent as they do when Fehling's method is employed. As their removal is attended with great difficulty, and they are usually present in small but constant amounts, we prefer not to undertake the purification of the urine, but to make an allowance equal to 0·2 per cent.,

equal to ·75 grains to the ounce of glucose, which must be subtracted from the total glucose found. That this correction is sufficiently exact for all ordinary purposes, we have proved by the comparative results yielded by a considerable number of diabetic and normal urines.

Johnson's Picric Acid Method.—The following solutions and apparatus are required :*

1. Standard solution of ferric acetate, equal in tint to that yielded by a solution of glucose containing 1 grain per fluid oz. This standard solution is prepared as follows :

Liquor ferri perchloridi fortior (P.B., sp. gr. 1·42)...	℥j.
Acidi acetici glacialis (P.B., sp. gr. 1·058)... ...	℥iv.
Liquor ammoniæ (P.B., sp. gr. 0·959)	℥ij.
Aqua distillata...	ad ℥iv.

Mix first the iron and the acid ; then add the ammonia, and water up to 4 fluid oz.

2. Saturated solution of picric acid, prepared by boiling the crystals with distilled water in the proportion of 6 grains to 1 fluid oz., and allowing the excess to crystallize out on cooling.

3. Liquor potassæ (P.B., specific gravity 1·058, 6 per cent.).

1. A tube about 12 inches in length, graduated into 100 cc., with longer divisions at each 10 cc., accurately stoppered and lipped.

2. A tube, half the above length and of equal diameter, accurately stoppered, to hold the standard solution.

3. A boiling-tube, 10 inches long, ¾ inch in diameter (internal), lipped, and graduated up to 4 fluid drachms.

4. 1 drachm measure.

Method of Performing the Estimation.—Measure 1 fluid drachm of urine into the boiling-tube. Add 1 fluid drachm of the saturated picric acid solution, and ½ fluid drachm of liquor potassæ. Make up to the 4-drachm mark on the tube with distilled or rain water. Heat over a spirit or gas lamp, and keep the liquid boiling for about a minute. Cool by dipping the tube after a minute in cold water, and ascertain that the cold liquid measures

* As this is a rapid method suitable for clinical purposes, we thought it best to give the pharmaceutical weights and measures, as the more ready to hand for medical purposes.

exactly 4 fluid drachms. If less, make up to the 4-drachm mark with distilled water; if more, evaporate down to the 4-drachm mark. If the colour of the boiled liquid is the same as that of the ferric acetate standard or paler, the urine is either free from sugar, or contains less than 1 grain per fluid oz. If the colour is paler than the standard, boil with 2 drachms of urine instead of 1, then divide the indicated reduction by 2. In analysing an undiluted urine the phosphates precipitated by the potash often cause turbidity, which must be removed by filtration before the colour can be accurately estimated. It should be borne in mind that all normal urines reduce picric acid to an extent equivalent to from $\frac{1}{2}$ grain to 1·2 grain of glucose per fluid oz. This reduction is due to kreatinine. This should be allowed for when the quantity of glucose present is very small. If the colour of the boiled liquid is darker than the standard, introduce it into the graduated tube until it stands at 10 divisions, whilst the stoppered tube at the side is filled with the ferric acetate standard. Now dilute the dark-red liquid in the graduated tube with distilled or rain water till the colour is the same as that of the standard. Each division above 10=0·1 grain per fluid oz. Thus, 13 division=1·3 grains, 30 division=3 grains per fluid oz., etc. If more than 6 grains per fluid oz. are indicated,* dilute the urine 10 times by pouring urine up to 10 divisions on the graduated tube, and distilled or rain water up to 100. Then analyse the diluted liquid as before. In this case each division on the saccharometer indicates 1 grain of sugar per fluid oz. Thus, diluting from 10 up to 48 divisions shows that the urine contains 48 grains of sugar per fluid oz. If the urine, when 10 times diluted, gives a colour paler than the standard, it contains less than 10 grains of sugar per fluid oz. Another portion should then be diluted 5 times by filling the graduated tube up to 10 divisions with urine, then up to 50 divisions with distilled or rain water.† The

* The reason for this is that 1 fl. drachm of picric acid solution is sufficient for the decomposition of not more than that proportion of sugar.

† The dilution of the urine may be more conveniently made by pouring 5 or 10 cc. into a 50 cc. flask and adding water up to the 50-cc. mark.

analysis is performed as before. The value of the divisions now will be half that with a 10 times diluted sample. Thus, 18 divisions would indicate 9 grains per fluid oz. If the urine has a specific gravity of 1035 or more it should be at once diluted 5 or 10 times before commencing an analysis.

The percentage weight of sugar to the volume of urine may be ascertained by dividing the number of grains per fluid oz. by 4·8.

The Estimation of Urea.—The urea is estimated by the hypobromite of sodium method, which depends on the fact that when urea is treated with a solution of hypobromite of sodium the urea is decomposed with the liberation of nitrogen, as shown by the following equation :

$$CH_4N_2O+3NaBrO=3NaBr+CO_2+2H_2O+N_2.$$

The whole of the nitrogen of the urea is not always evolved, while some of the nitrogen may be yielded by the other nitrogenous constituents of the urine—for instance, uric acid, kreatinine, etc. This is of but little consequence, as a given specimen always yields the same quantity of gas.

The process is carried out as follows : 25 cc. of the sodium hypobromite solution (made by adding 2·5 cc. of bromine to 25 cc. of 40 per cent. soda hydrate and cooling) is placed in a 4-oz bottle fitted with a rubber stopper, through which passes a glass tube, to which is attached an indiarubber tube, the other end of which is connected with a nitrometer. Into the bottle containing the hypobromite solution is lowered a short test-tube containing 5 cc. of the urine, taking great care that none is spilt. The bottle is then carefully corked and connected with the nitrometer, which is best filled with water. The water-level is then set, and the generating bottle tilted, when, the urine mixing with the hypobromite solution, nitrogen and carbon dioxide will be evolved according to the equation already given, the carbon dioxide being absorbed by the excess of caustic soda present. After a few minutes the water-levels in the two tubes of the nitrometer are adjusted, and the increased volume of gas due to nitrogen noted. Each cc. of nitrogen at the normal temperature and pressure equals ·0029 grammes of urea in the 5 cc. of urine tested.

Normal urine contains from 2 to 3 per cent. urea.

The Determination of Uric Acid. — Uric acid is detected in urine by the addition of one-fifth of its volume of concentrated hydrochloric acid. The uric acid will deposit after standing some hours in the form of reddish-brown crystals. Uric acid can be estimated by Haycraft's method, which is based on the fact that uric acid combines with silver as silver urate, which is practically insoluble in water, ammonia, or acetic acid, but perfectly soluble in nitric acid. The estimation of the uric acid depends upon the titration of the silver, which is combined by Volhard's method. The necessary solutions are :

(*a*) A centinormal solution of ammonium thiocyanate, standardized by a silver solution of known strength. 1 cc. of this=0·00168 gramme uric acid.

(*b*) An ammoniacal silver solution. 5 grammes silver nitrate in about 100 cc. of water, precipitated and re-dissolved in ammonia to a clear solution.

(*c*) Ferric indicator. A saturated solution of iron alum.

(*d*) Pure nitric acid. 25 cc. of the urine is placed in a small beaker, together with about 1 gramme of sodium bicarbonate, and two or three drops of strong ammonia. This precipitates ammonio-magnesic phosphate, and prevents reduction of silver ; 1 to 2 cc. of ammoniacal silver solution is then added, which at once precipitates the silver urate. The mixture is now placed on a filter, and washed until the washings show no trace of silver on testing with salt solution. The precipitate is then dissolved in a few cc.'s of nitric acid, washed into a flask, a few drops of the ferric indicator added, and then titrated with the ammonium thiocyanate solution until a permanent red colour just appears. The number of cc.'s used, multiplied by 0·00168×4, gives the percentage of uric acid in the sample. (Sutton, 'Vol. Analysis.')

Normal urine contains from 0·3 to 0·7 per cent. uric acid.

The Detection of Bile.—*Pettenkofer's Test.*—Equal parts of the urine and sulphuric acid are mixed ; after cooling the tube in cold water, a little powdered white sugar is then added ; after well mixing, the tube is slightly warmed. If a reddish or violet coloration due to the liberation of cholalic acid is seen, bile is undoubtedly present.

Gmelin's Test.—When urine containing bile is cautiously mixed with an equal volume of nitric acid, a play of colours is seen, varying from green or blue to violet and red.

Oliver's Test.—1 cc. of the clear urine (which is filtered if necessary) is mixed with 3 cc. of Oliver's reagent. An opalescence appears if bile acids are present.

Oliver's reagent is made as follows: 2 grammes of peptone, 0·25 gramme salicylic acid, are dissolved in water, to which 2 cc. of 33 per cent. acetic acid had been added. The solution is diluted to 200 cc. The reagent must be rendered perfectly bright by filtration before using.

The Detection of Blood. — Urine containing blood generally has a characteristic smoky appearance. The urine may be examined by Dr. Day's test as follows: 2 or 3 cc. of tincture of guaiacum (which must be freshly made from the unoxidized resin), and a like amount of an ethereal solution of peroxide of hydrogen (ozonic ether), are added to the urine or the deposit. In the presence of blood, a beautiful sapphire blue colour will develop.

Note.—This test must be regarded with caution, as many other organic bodies yield a similar reaction.

Estimation of Phosphoric Acid.—After removal of albumen, if present, by boiling, 100 cc. of the urine is boiled with an excess of nitric acid; ammonium molybdate and ammonium nitrate, dissolved in nitric acid, is then added, the liquid well boiled, and allowed to stand some hours. The precipitate is filtered off, and washed with dilute alcohol until free from acidity. The precipitate is then redissolved in ammonia and a solution of ammonio-sulphate of magnesium (magnesia mixture), and allowed to stand over-night. The precipitate is collected on a filter, and washed with a mixture of one volume of ammonia and three of water. The precipitate is now ignited, allowed to cool, moistened with nitric acid, dried, and again ignited before the blowpipe. The magnesium pyrophosphate ($Mg_2P_2O_7$) is then weighed, the weight multiplied by the factor ·63964 to obtain the amount of P_2O_5.

Normal urine contains from 0·2 to 0·3 per cent. of P_2O_5.

Estimation of Sulphates.—100 cc. of the urine, free from albumen, is acidulated with hydrochloric acid, boiled, and barium chloride added; the liquid again well boiled, and the precipitated barium sulphate filtered off, the filter

well washed, dried, ignited, and weighed in the usual way. The weight of barium sulphate obtained is multiplied by the factor ·34335 to obtain the amount of SO_3 present.

Normal urine contains from 0·15 to 0·3 per cent. SO_3.

Estimation of Chlorides.—10 cc. of the urine is very carefully neutralized with sodium carbonate, and then diluted to 100 cc. 10 cc. are then taken and diluted to about 100 cc. in a white dish, one or two drops of pure neutral chromate of potassium solution added, and the solution titrated with decinormal silver nitrate, when ·00585 × cc. used × 100 = per cent. NaCl present.

Normal urine contains from 0·5 to 1·0 per cent. of sodium chloride.

Chemical Examination of the Sediment. — The urine is allowed to deposit in a conical test-glass, and the deposit examined both chemically and microscopically. Urinary deposits are generally simple in character, and their composition can usually be determined by the following tests:

1. Warm the urine containing the sediment, when if the latter should dissolve, it consists entirely of urates. In this case, let it once more crystallize out, and examine it by the ordinary course for Ca, Na, and NH_4 to ascertain the bases.

2. If the deposit be not dissolved by heating, let it settle, wash once by decantation with cold water, and warm with acetic acid. Phosphates will dissolve, and may be reprecipitated from the solution by excess of ammonia filtered out, well washed with boiling water, dissolved in acetic acid, and examined for Ca or Mg by the usual course for these metals in presence of phosphoric acid.

3. If the deposit is insoluble in acetic acid, warm it with hydrochloric acid. Any soluble portion is calcium oxalate, which may be precipitated by ammonia.

4. If the deposit is insoluble in hydrochloric acid, it is in all probability uric acid. In this case apply the 'Murexid' test as follows: Place it in a small white dish, remove moisture by means of filter paper, add a drop or two of strong nitric acid, and evaporate to dryness at a gentle heat. When cold, add a drop of ammonia, which will produce a purple colour, deepened to violet by a drop of caustic potash solution.

The urates are often of a pinkish colour, owing to the presence of the red pigment 'purpurin,' whence the name 'red gravel.' Phosphate of calcium and the ammonio-magnesium phosphate are generally both present in deposits, the magnesium salt usually forming the larger proportion. Free uric acid is nearly always crystalline, and yellow, red, or brown in colour.

Microscopical Examination of the Sediment.—The microscopical examination of urinary deposits requires much experience to be of value. In case of doubt, reference should always be made to typical slides. The best magnification to use is about sixty diameters. The following are the general characters of the most frequent forms :

Ammonio-Magnesium Phosphate (*Triple Phosphate*).—This is deposited as soon as the urine becomes alkaline, the ammonia being derived from the decomposition of the urea. The crystals are seen as regular and ragged stellate plates. Arborescent forms are also sometimes seen.

Uric acid occurs in flat plates, quadratic prisms, needles, rosettes ; spindle and star-like crystals are also of frequent occurrence. On testing with a drop of potash inserted under the cover-glass, uric acid will dissolve.

Amorphous deposits may be either phosphate of magnesium or calcium, or the urates of calcium, magnesium, ammonium, potassium, or sodium, chiefly the last. The urates may be detected by treatment on the slide with acetic acid, when in the case of the urates the characteristic forms of uric acid will develop.

The urates of magnesium and sodium sometimes occur crystalline in the form of small tufts or bundles of needles.

Oxalate of calcium occurs in very small octahedra. Oxalate of calcium is insoluble in acetic acid, but soluble in hydrochloric acid.

Cystin is somewhat rare as a urinary deposit ; it is seen in the form of flat hexagonal lamellæ superposed. Cystin is soluble in ammonia.

Hippuric acid occurs in characteristic pointed rhombic prisms and acicular crystals. The larger crystals may be mistaken for triple phosphate, and the smaller for uric acid ; but insolubility in acetic acid distinguishes them from the former, and solubility in alcohol from the latter.

Blood is easily recognised by the reddish circular

corpuscles ; the discs are seen, both singly and in strings, not unlike piles of coins. In stale urine, the blood corpuscles lose their round shape, and become angular.

Pus deposits on standing as a light-coloured layer, which easily diffuses through the liquid on shaking. Pus corpuscles are larger than those of blood, and are light coloured.

Mucus deposits not unlike pus, but has no definite structure ; it generally occurs with pus epithelium, etc. Mucus imparts a 'ropy' appearance to urine.

Epithelial debris are frequently present in urine in the form of nucleated cells, regular and oval when full, but angular and unsymmetrical when partially emptied of their contents.

Casts of uriniferous tubuli are fibrinous masses of various forms, and often of considerable length ; sometimes delicate and transparent, occasionally granular, and often containing fat globules.

Spermatozoa are liable to escape notice, on account of their extremely small size and transparency. Their tadpole-like appearance is characteristic.

Various micro-organisms are frequently met with in urine. *Sarcina*, *staphylococcus pyogenes aureus*, various *streptococci*, the *gonococcus*, etc., are those of frequent occurrence. Staining with aniline-gentian-violet will render their recognition more easy.

Foreign bodies, such as hair, fibres of wool and cotton, fragments of feathers, are amongst those most frequently seen, but are not easily mistaken for any substances that can actually occur in urine.

ALCOHOL TABLES.

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
1·0000	0·00	0·00	0·00	·9689	22·15	27·04	47·39
·9999	0·05	0·07	0·12	·9679	22·92	27·95	48·98
·9989	0·58	0·73	1·28	·9669	23·69	28·86	50·57
·9979	1·12	1·42	2·48	·9659	24·46	29·76	52·16
·9969	1·75	2·20	3·85	·9649	25·21	30·65	53·71
·9959	2·33	2·93	5·13	·9639	25·93	31·48	55·18
·9949	2·89	3·62	6·34	·9629	26·60	32·27	56·55
·9939	3·47	4·34	7·61	·9619	27·29	33·06	57·94
·9929	4·06	5·08	8·90	·9609	28·00	33·89	59·40
·9919	4·69	5·86	10·26	·9599	28·62	34·61	60·66
·9909	5·31	6·63	11·62	·9589	29·27	35·35	61·95
·9899	5·94	7·40	12·97	·9579	29·93	36·12	63·30
·9889	6·64	8·27	14·50	·9569	30·50	36·76	64·43
·9879	7·33	9·13	15·99	·9559	31·06	37·41	65·55
·9869	8·00	9·95	17·43	·9549	31·69	38·11	66·80
·9859	8·71	10·82	18·96	·9539	32·31	38·82	68·04
·9849	9·43	11·70	20·50	·9529	32·94	39·54	69·29
·9839	10·15	12·58	22·06	·9519	33·53	40·20	70·46
·9829	10·92	13·52	23·70	·9509	34·10	40·84	71·58
·9819	11·69	14·46	25·34	·9499	34·57	41·37	72·50
·9809	12·46	15·40	26·99	·9489	35·05	41·90	73·43
·9799	13·23	16·33	28·62	·9479	35·55	42·45	74·39
·9789	14·00	17·26	30·26	·9469	36·06	43·01	75·37
·9779	14·91	18·36	32·19	·9459	36·61	43·63	76·45
·9769	15·75	19·39	33·96	·9449	37·17	44·24	77·53
·9759	16·54	20·33	35·63	·9439	37·72	44·86	78·61
·9749	17·33	21·29	37·30	·9429	38·28	45·47	79·68
·9739	18·15	22·27	39·03	·9419	38·83	46·08	80·75
·9729	18·92	23·19	40·64	·9409	39·35	46·64	81·74
·9719	19·75	24·18	42·38	·9399	39·85	47·18	82·69
·9709	20·58	25·17	44·12	·9389	40·35	47·72	83·64
·9699	21·38	26·13	45·79	·9379	40·85	48·26	84·58

ALCOHOL TABLES—*continued.*

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
·9369	41·35	48·80	85·53	·9079	54·52	62·36	109·28
·9359	41·85	49·34	86·47	·9069	55·00	62·84	110·12
·9349	42·33	49·86	87·37	·9059	55·45	63·28	110·92
·9339	42·81	50·37	88·26	·9049	55·91	63·73	111·71
·9329	43·29	50·87	89·15	·9039	56·36	64·18	112·49
·9319	43·76	51·38	90·03	·9029	56·82	64·63	113·26
·9309	44·23	51·87	90·89	·9019	57·25	65·05	113·99
·9299	44·68	52·34	91·73	·9009	57·67	65·45	114·69
·9289	45·14	52·82	92·56	·8999	58·09	65·85	115·41
·9279	45·59	53·29	93·39	·8989	58·55	66·29	116·18
·9269	46·05	53·77	94·22	·8979	59·00	66·74	116·96
·9259	46·50	54·24	95·05	·8969	59·43	67·15	117·68
·9249	46·96	54·71	95·88	·8959	59·87	67·57	118·41
·9239	47·41	55·18	96·70	·8949	60·29	67·97	119·12
·9229	47·86	55·65	97·52	·8939	60·71	68·36	119·80
·9219	48·32	56·11	98·34	·8929	61·13	68·76	120·49
·9209	48·77	56·58	99·16	·8919	61·54	69·15	121·18
·9199	49·20	57·02	99·93	·8909	61·96	69·54	121·86
				·8899	62·41	69·96	122·61
·9198	49·24	57·06	100·00P.s.	·8889	62·86	70·40	123·36
				·8879	63·30	70·81	124·09
·9189	49·68	57·49	100·76	·8869	63·74	71·22	124·80
·9179	50·13	57·97	101·59	·8859	64·17	71·62	125·51
·9169	50·57	58·41	102·35	·8849	64·61	72·02	126·22
·9159	51·00	58·85	103·12	·8839	65·04	72·42	126·92
·9149	51·42	59·26	103·85	·8829	65·46	72·80	127·59
·9139	51·83	59·68	104·58	·8819	65·88	73·19	128·25
·9129	52·27	60·12	105·35	·8809	66·30	73·57	128·94
·9119	52·73	60·56	106·15	·8799	66·74	73·97	129·64
·9109	53·17	61·02	106·93	·8789	67·17	74·37	130·33
·9099	53·61	61·45	107·69	·8779	67·58	74·74	130·98
·9089	54·05	61·88	108·45	·8769	68·00	75·12	131·64

ALCOHOL TABLES—*continued.*

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
·8759	68·42	75·49	132·30	·8439	81·80	86·96	152·40
·8749	68·83	75·87	132·95	·8429	82·19	87·27	152·95
·8739	69·25	76·24	133·60	·8419	82·58	87·58	153·48
·8729	69·67	76·61	134·25	·8409	82·96	87·88	154·01
·8719	70·08	76·98	134·90	·8399	83·35	88·19	154·54
·8709	70·48	77·32	135·51	·8389	83·73	88·49	155·07
·8699	70·88	77·67	136·13	·8379	84·12	88·79	155·61
·8689	71·29	78·04	136·76	·8369	84·52	89·11	156·16
·8679	71·71	78·40	137·40	·8359	84·92	89·42	156·71
·8669	72·13	78·77	138·05	·8349	85·31	89·72	157·24
·8659	72·57	79·16	138·72	·8339	85·69	90·02	157·76
·8649	73·00	79·54	139·39	·8329	86·08	90·32	158·28
·8639	73·42	79·90	140·02	·8319	86·46	90·61	158·79
·8629	73·83	80·26	140·65	·8309	86·85	90·90	159·31
·8619	74·27	80·64	141·33	·8299	87·23	91·20	159·82
·8609	74·73	81·04	142·03	·8289	87·62	91·49	160·33
·8599	75·18	81·44	142·73	·8279	88·00	91·78	160·84
·8589	75·64	81·84	143·42	·8269	88·40	92·08	161·37
·8579	76·08	82·23	144·10	·8259	88·80	92·39	161·91
·8569	76·50	82·58	144·72	·8249	89·19	92·68	162·43
·8559	76·92	82·93	145·34	·8239	89·58	92·97	162·93
·8549	77·33	83·28	145·96	·8229	89·96	93·26	163·43
·8539	77·75	83·64	146·57	·8219	90·32	93·52	163·88
·8529	78·16	83.98	147·17	·8209	90·68	93·77	164·33
·8519	78·56	84·31	147·75	·8199	91·04	94·03	164·78
·8509	78·96	84·64	148·32	·8189	91·39	94·28	165·23
·8499	79·36	84·97	148·90	·8179	91·75	94·53	165·67
·8489	79·76	85·29	149·44	·8169	92·11	94·79	166·12
·8479	80·17	85·63	150·06	·8159	92·48	95·06	166·58
·8469	80·58	85·97	150·67	·8149	92·85	95·32	167·04
·8459	81·00	86·32	151·27	·8139	93·22	95·58	167·50
·8449	81·40	86·64	151·83	·8129	93·59	95·84	167·96

ALCOHOL TABLES—*continued.*

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
·8119	93·96	96·11	168·24	·7999	98·06	98·82	173·17
·8109	94·31	96·34	168·84	·7989	98·37	99·00	173·50
·8099	94·66	96·57	169·24	·7979	98·69	99·18	173·84
·8089	95·00	96·80	169·65	·7969	99·00	99·37	174·17
·8079	95·36	97·05	170·07	·7959	99·32	99·57	174·52
·8069	95·71	97·29	170·50	·7949	99·65	99·77	174·87
·8059	96·07	97·53	170·99	·7939	99·97	99·98	175·22
·8049	96·40	97·75	171·30				
·8039	96·73	97·96	171·68		Absolute Alcohol.		
·8029	97·07	98·18	172·05				
·8019	97·40	98·39	172·43				
·8009	97·73	98·61	172·80	·7938	100·00	100·00	175·25

Alcohol Calculations.—Proof spirit is defined by Act of Parliament to be a liquid of such a density that at 51° F. 13 volumes shall be equal in weight to 12 volumes of water of the same temperature. Such a spirit has a density of ·91984 at 60° F., and contains 49·24 per cent. by weight of alcohol and 50·76 of water. Spirits weaker than this are said to be *under* proof, U P ; when stronger *over* proof, O P. A spirit is said to be 20 degrees or 20 per cent. under proof when it contains at 60° F. 80 measures of proof spirit and 20 of water ; and 50° O P when 100 measures at 60° F. would require to be diluted to 150 measures to form proof spirit.

To find the percentage of alcohol by volume, multiply the percentage of alcohol by weight by the observed specific gravity, divide the product by ·7938.

Ex. $\frac{\cdot 8979 \times 59}{\cdot 7938} = 66\cdot 74$ per cent. of alcohol per volume.

To find the percentage volume of proof spirit multiply the percentage of alcohol by volume contained in the samples by 1·7525. Ex. 66·74 × 1·7525 = 116·96, or we may divide by ·5076 instead of multiplying by 1·7525.

Suppose it is required to find what proportion of proof, or any other strength of spirit a particular sample of alcohol contains or would contain when diluted, proceed as follows :

$$\frac{\text{P.C. of proof spirit in alcohol required} \times 100}{\text{P.C. of proof spirit in sample.}} = \left\{\begin{array}{l}\text{The number of vols. of the stronger spirit which will produce or be contained in 100 measures of the dilute spirit.}\end{array}\right.$$

Required the percentage of gin at 35° U P contained in a watered sample of 44° U P.

$$\frac{56 \times 100}{65} = 86{\cdot}15 \text{ per cent. per volume.}$$

Required the proportion of water which must be added to spirit of 25° O P to reduce it to 20° U P.

$\frac{80 \times 100}{125} = 64$. Hence 64 measures at 25° O P must be diluted to 100 to obtain a spirit of 20° U P.

To reduce spirit to a required strength. If the proof strength is known, note that each degree above proof of the dilution required *plus* 100 is the factor to start with. Thus, if we want to reduce 60° O P spirit to 20° O P, we take 120 volumes of the 60° O P, and add water to make it 160 volumes. If only the specific gravity is known, refer to our alcohol tables, and compare the overproof with the specific gravity, when the sum can be worked out. The following are some of the more useful figures in that connection :

Specific Gravity.	Percentage of Proof Spirit.
0·829	160 or 60° O P.
0·833	158 „ 58° „
0·837	156 „ 56° „
0·8405	154 „ 54° „
0·8475	150 „ 50° „
0·856	145 „ 45° „
0·864	140 „ 40° „
0·872	135 „ 35° „
0·886	125 „ 25° „
0·9005	115 „ 15° „
0·907	110 „ 10° „
0·920	100 „ proof

Owing to the contraction of volume when alcohol and water are mixed, there is no regular increment of difference in the relation between the degrees and the specific gravities. This is evident from the above figures, but the following are approximately correct factors :

There is an increase in specific gravity of

0·0018	for each	degree	between	60°	and	50° O P.
0·0017	„	„		50°	„	40° „
0·0015	„	„		40°	„	30° „
0·00147	„	„		30°	„	20° „
0·00137	„	„		20°	„	10° „
0·0013	„	„		10°	„	0° „

With the aid of the factors in the first column it will be possible to work out the above rule without referring to an alcohol table. Were it not for the contraction which occurs when water and alcohol are mixed, the following rule as to mixtures of liquids of different specific gravity could be used with certainty. The object of the rule is to determine what proportions of two liquids differing in density must be taken to produce a liquid of a required density.

Let the specific gravity of the lighter liquid be A, *the specific gravity of the heavier* B, *and the required specific gravity* C, *then—*

C – A = volume of B to be taken.
B – C = volume of A to be taken.

If strict exactitude is not required, the rule may be used for spirit mixtures, ammonia solution and water, etc.

CORRECTION FOR TEMPERATURE in specific gravity of mixtures of alcohol and water can be determined from the following formula :

$$w = w' \pm t \left(\cdot 00014 \times \frac{1 - w'}{150} \right)$$

Where w' = the observed density
w = the density at 15·5° C.
t = the difference between the normal and observed temperatures in degrees Centigrade
·00014 = the coefficient of expansion for alcohol.

The + sign is used if the temperature of the experiment is above 15·5° C. ; the – sign if below that point.

THERMOMETRIC SCALES.—To convert Fahrenheit-heat degrees to Centigrade terms, subtract 32, multiply by 5, and divide by 9.

To convert Centigrade degrees into Fahrenheit multiply by 9, divide by 5, and add 32.

°C. °F.	°C. °F.	°C. °F.	°C. °F.
1=33·8	14=57·2	27= 80·6	40=104·0
2=35·6	15=59·0	28= 82·4	41=105·8
3=37·4	16=60·8	29= 84·2	42=107·6
4=39·2	17=62·6	30= 86·0	43=109·4
5=41·0	18=64·4	31= 87·8	44=111·2
6=42·8	19=66·2	32= 89·6	45=113·0
7=44·6	20=68·0	33= 91·4	46=114·8
8=46·4	21=69·8	34= 93·2	47=116·6
9=48·2	22=71·6	35= 95·0	48=118·4
10=50·0	23=73·4	36= 96·8	49=120·2
11=51·8	24=75·2	37= 98·6	50=122·0
12=53·6	25=77·0	38=100·4	51=123·8
13=55·4	26=78·8	39=102·2	52=125·6

WEIGHTS AND MEASURES OF THE METRICAL SYSTEM.

Weights.

1 Milligramme = the thousandth part of one gramme or 0·001 gramme.
1 Centigramme = the hundredth part of one gramme or 0·01 gramme.
1 Decigramme = the tenth part of one grm. or 0·1 grm.
1 Gramme = weight of a cubic centimetre of 1·0 „ water at 4° C.
1 Decagramme = ten grammes „ 10·0 „
1 Hectogramme = one hundred grms. „ 100·0 „
1 Kilogramme = one thousand grms. „ 1000·0 „

Measures of Capacity.

1 Millilitre = 1 cub. centim. or the mea. of 1 grm. of water
1 Centilitre = 10 „ 10 „ „
1 Decilitre = 100 „ 100 „ „
1 Litre = 1000 „ 1000 „ (1 kilo.)

Measures of Length.

1 Millimetre = the thousandth part of one metre or 0·001 metre.
1 Centimetre = the hundredth part of one metre or 0·01 metre.
1 Decimetre = the tenth part of one metre or 0·1 metre.
1 Metre = the ten-millionth part of a quarter of the meridian of the earth.

Relation of the Weights of the British Pharmacopœia to the Metrical Weights.

1 Pound = 453·5925 grammes
1 Ounce = 28·3495 „
1 Grain = 0·0648 „

Relation of Measures of Capacity of the British Pharmacopœia to the Metrical Measures.

1 Gallon	=4·543487	litres		
1 Pint	=0·567936	,,	or 567·936	cub. centims.
1 Fluid Ounce	=0·028396	,,	28·396	,,
1 Fluid Drachm	=0·003549	,,	3·549	,,
1 Minim	=0·000059	,,	0·059	,,

Relation of the Metrical Weights to the Weights of the British Pharmacopœia.

1 Milligramme	=	0·015432	grs.
1 Centigramme	=	0·15432	,,
1 Decigramme	=	1·5432	,,
1 Gramme	=	15·432	,,
1 Kilogramme	=2 lb. 3 oz. 119·8 grs.	or 15432·348	,,

Relation of the Metrical Measures to the Measures of the British Pharmacopœia.

1 Millimetre	=	0·03937	inch
1 Centimetre	=	0·39371	,,
1 Decimetre	=	3·93708	inches
1 Metre	=39·37079	,,	or 1 yard 3·7 inches

1 Cubic centimetre	=	15·432 grain-measures
1 Litre	=1 pint 15 oz. 2 dr. 11 m.	or 15432·348 grain-measures

CO-EFFICIENTS REQUIRED IN VOLUMETRIC ANALYSIS.

Normal Acid Solution.

Oxalic acid	·063
Sulphuric acid	·049
NH_3	·017
NH_4HO	·035
NH_4HCO_3 . $NH_4NH_2CO_2$	·0523
$Na_2B_4O_7$. $10H_2O$	·191
Ca2HO	·037
CaO	·028
$CaCO_3$	·05
$Ba(HO)_2$	·0855
$Ba(HO)_28H_2O$	·1575
$BaCO_3$	·0985
MgO	·02
$MgCO_3$	·042
KHO	·056
K_2CO_3	·069
$K_2C_4H_4O_6$ (converted into K_2CO_3)	·113
$KHC_4H_4O_6$	·188
$K_3C_6H_5O_7$	·102
$KC_2H_3O_2$	·098
NaHO	·04
Na_2CO_3	·053
Na_2CO_3 . $10H_2O$	·143
$NaHCO_3$	·084

Normal Soda Solution.

Sodium hydrate	·04
$HC_2H_3O_2$ (acetic)	·06
$H_3C_6H_5O_7H_2O$ (citric)	·07
HCl	·0365
HBr	·081
HI	·128
HNO_3	·063
H_2SO_4	·049
$H_2C_4H_4O_6$ (tartaric)	·075
$HC_3H_5O_3$ (lactic)	·09
$H_2C_2O_42H_2O$ (oxalic)	·063

$\frac{N}{10}$ Nitrate of Silver Solution.

Argentic nitrate	·017
CN	·0052
HCN	·0054
KCN	·01302
NH_4Cl	·00535
KCl	·00745
NaCl	·00585
KBr	·0119
NaBr	·0103
Cl	·00355

$\frac{N}{10}$ Iodine Solution.

Iodine	·0127
SO_2	·0032
H_2SO_3	·0041
As_2O_3	·00495
$Na_2S_2O_35H_2O$	·0248
$Na_2SO_37H_2O$	·0126
$K_2SO_32H_2O$	·0097

$\frac{N}{20}$ Bichromate of Potassium.

Potassium bichromate	·01475
Fe (ferrous)	·0168
$FeSO_4$	·0456
$FeSO_42H_2O$	·0564
$FeSO_47H_2O$	·0834
$Fe_3(AsO_4)_2$	·0446
$Fe_3(PO_4)_2$	·0358
$FeCO_3$	·0348
Fe_3O_4	·0696
FeO	·0216

$\frac{N}{10}$ Hyposulphite of Soda Solution.

Hyposulphite of sodium	·0248
I	·0127
Cl	·00355
Br	·0080

$\frac{N}{10}$ Permanganate of Potassium.

Potassium permanganate	·00316
Fe (ferrous)	·0056
$FeSO_4$	·0152
$FeSO_4 . 7H_2O$	·0278
$FeCO_3$	·0116
FeO	·0072
$H_2C_2O_4 2H_2O$	·0063
$CeC_2O_4 . 9H_2O$	·354

Standard Fehling's Solution.

(10 cc. used.)

Glucose	·05
Cane sugar (after inversion)	·0475
Maltose	·082
Lactose	·0714
Starch (after conversion)	·045

Nitrometer Analysis.

Each cc. of NO at N.T.P. equals gramme of	·00281	HNO_3
	·00241	N_2O_5
	·00450	KNO_3
	·00334	$C_2H_5 . NO$
	·0026	Urea
Each cc. of CO_2 at N.T.P. equals gramme of	·0042	$(NH_4)_2CO_3$
	·001967	CO_2

Nitrogen × by factor 6·33 = Albuminoids.

USEFUL DATA.

1 metre=39·37 inches, or 1 yard and $3\frac{1}{3}$ inches (nearly).
25 millimetres=1 inch (nearly).
30 centimetres=1 foot (nearly).
8 kilometres=5 miles (nearly).
$6\frac{1}{2}$ square centimetres=1 square inch (nearly).
$9\frac{1}{4}$ square decimetres=1 square foot (nearly).
1 kilogramme=15432·3 grains, or 2·2 pounds (nearly).
28 grammes=1 ounce avoirdupois (nearly).
455 grammes=1 pound avoirdupois (nearly).
65 milligrammes=1 grain (nearly).
1 litre=35·2 ounces, or 1·76 pints (nearly).
100 cubic centimetres=$3\frac{1}{2}$ ounces (nearly).
1 cubic centimetre=15·4 grains, or 16·7 minims (nearly).
1 cubic inch=16·4 cubic centimetres (nearly).
1 gallon=4·5 litres (nearly).

Cubic feet × 6·2355=gallons.
Cubic inches × ·003607=gallons.
To reduce ounces to grammes, multiply by 28·349.
To reduce grains to grammes, multiply by ·0648.
To reduce grammes to grains, multiply by 15·432.
To reduce pints to cubic centimetres, multiply by 567·936.
To reduce gallons to litres, multiply by 4·548.
To reduce litres to gallons, multiply by ·22.
To reduce kilogrammes to pounds, multiply by 2·2046.
To reduce centimetres to inches, multiply by ·3937.
To reduce inches to centimetres, multiply by 2·54.
To convert degrees Twaddle into specific gravity + 5, and add 1,000.
To convert grammes per 100 cubic centimetres to grains per fluid ounce, multiply by 4·375.
To convert grammes per 100 cubic centimetres to grains per gallon, multiply by 700.
To convert parts per million into grains per gallon × ·07.
To convert grains per gallon into parts per million ÷ ·07
To convert parts per 100,000 into parts per million × 100.
To convert grains per gallon (=parts per 70,000) into parts per 100,000 ÷ ·7.

ATOMIC WEIGHTS OF THE ELEMENTS.

Element.	Symbol and Atomicity.	Atomic Weight.
Aluminium	Al III. IV.	27·5
Antimony	Sb III. V.	120
Arsenic	As III. V.	75
Barium	Ba II.	137
Beryllium	Be II. III.	9·4
Bismuth	Bi III. V.	208
Boron	Bo III. V.	11
Bromine	Br I. III. V. VII.	80
Cadmium	Cd II.	112
Cæsium	Cs I.	133
Calcium	Ca II.	40
Carbon	C IV. II.	12
Cerium	Ce III. IV.	138
Chlorine	Cl I. III. V. VII.	35·5
Chromium	Cr IV. VI.	52·5
Cobalt	Co II. IV.	59
Copper	Cu II.	63
Didymium	Di IV.	145
Erbium	E II.	169
Fluorine	F I.	19
Gallium	Ga IV.	69
Gold	Au I. III.	196·7
Hydrogen	H I.	1
Indium	In III.	113·4
Iodine	I I. III. V. VII.	127
Iridium	Ir II. IV. VI.	193
Iron	Fe II. IV. VI.	56
Lanthanum	La IV.	139
Lead	Pb II. IV.	207
Lithium	Li I.	7
Magnesium	Mg II.	24
Manganese	Mn II. IV. VI. VII.	55
Mercury	Hg II.	200
Molybdenum	Mo VI.	96

ATOMIC WEIGHTS OF THE ELEMENTS—

continued.

Element.	Symbol and Atomicity.	Atomic Weight.
Nickel	Ni II. IV.	58·8
Niobium	Nb V.	94
Nitrogen	N III. V.	14
Osmium	Os II. IV. VI. VIII.	199
Oxygen	O II.	16
Palladium	Pd II. IV. VI.	106·5
Phosphorus	P III. V.	31
Platinum	Pt II. IV. VI.	197·18
Potassium	K I.	39
Rhodium	Rh II. IV. VI.	104
Rubidium	Rb I.	85
Ruthenium	Ru II. IV. VI. VIII.	104
Selenium	Se II. IV. VI.	79
Silicon	Si IV.	28
Silver	Ag I.	108
Sodium	Na I.	23
Strontium	Sr II.	87·5
Sulphur	S II. IV. VI.	32
Tantalum	Ta V.	182
Tellurium	Te II. IV. VI.	128
Thallium	Tl I. III.	204
Thorium	Th IV.	231·5
Tin	Sn IV.	118
Titanium	Te IV.	48
Tungsten	W IV. VI.	184
Uranium	U VI. IV.	240
Vanadium	V III. V.	51·2
Yttrium	Y IV.	89
Zinc	Zn II.	65
Zirconium	Zr IV.	90

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THE END.

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