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Aids to The Analysis of Food and Drugs

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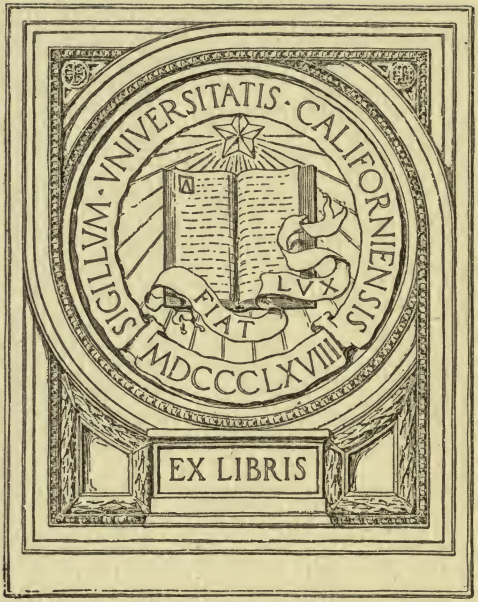
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AIDS TO THE ANALYSIS OF FOOD AND DRUGS

AIDS

TO

THE ANALYSIS OF FOOD AND DRUGS

BY

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AND

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FOURTH EDITION

NEW YORK

WILLIAM WOOD AND COMPANY

MDCCCCXVIII

PRINTED IN GREAT BRITAIN

PREFACE TO FOURTH EDITION

In this book we attempt to present in compact form information dealing with the analysis of food and of such drugs as are commonly sold to the public.

Since the publication of the third edition, few really new methods of analysis have appeared, but a large number of processes then known, but little used, have come into frequent employment. In addition, fresh Regulations, Orders, and recommendations, of Government departments have been issued, foods and food adjuncts from new sources have appeared, closer attention has been given to impurities, and many more novel adulterants are employed. The various monographs have been revised to comprehend these and other modern developments and requirements.

Among the processes now described are those for the facing of grains, starch in sausages, catalase in milk, the Kirschner process, and methods for the detection and estimation of sulphites, benzoates, hydrogen peroxide, and other preservatives. Some hitherto unpublished work is also given.

Many methods have been replaced by others: we now give Fiehe's test for invert sugar, Evers's process for arachidic acid, Tatlock and Thomson's process for caffeine, and the English process for fibre.

A monograph on Cider has been added. Among the new sections are those on the freezing-point of milk, milk enzymes, flour 'improvers,' self-raising flour, bleaching of flour, hardened oils, dirt in milk, and unsound fruit in jam. Much additional information on poisonous metals

is given, and processes for the estimation of traces of lead, arsenic, zinc, and copper are described, including the Pharmacopœial 'quantitative-limit' tests for the first two.

Of the civilised nations, Great Britain has fewest bureaucratic directions on the criteria to be used in determining the purity of food. References to colonial and foreign legislation, 'standards,' tariff regulations, and customs requirements, are given. These are useful if read as the tentative opinions of others. But as some foreign standards are rescinded or altered at intervals, comparisons should be made with discretion. Such legal decisions as have altered the complexion of various forms of adulteration are also given.

So much information is obtained nowadays from the analysis of urine, that a satisfactory revision would add seriously to the bulk of this book. We have deleted this section in the hope that at some time or other it may be the subject of a new volume in the 'Aids' series. The monograph on infants' foods has been deleted, and the subject of human milk more fully dealt with instead.

As a result of the prolongation of the war, the compositions of many articles have been changed. Though we try to enumerate the alterations in the Appendix (to which reference should be made before reporting on any food or drug), it is possible that we do not know of all the Food Controller's Orders concerned.

The new edition of the British Pharmacopœia contains many big alterations and a host of minor ones. This has involved the 'scrapping' of much of the material we had accumulated for this book, and lack of time has interfered with the preparation of as much information to replace it as we wanted. All the same, this section has been extended and some information on Pharmacopœial requirements is distributed through other chapters.

The Pharmacopœial list of alterations, though adequate for prescribing purposes, is insufficient for the guidance of the analyst. Many tinctures, powders, and other articles not mentioned therein are sufficiently different in composition from those going by the same names in the 1898 edition to show marked changes in the analytical data. When consulting figures obtained before 1915, it is imperative to compare, not only the relative proportions, but also the composition of each separate constituent, of a compounded drug. In this connection, the interpolations of 'Modified' and 'Altered' in Squire's 'Companion' are helpful.

We gratefully acknowledge the assistance of Mr. E. M. Hawkins, F.I.C., in reading our manuscript and making valuable suggestions.

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April 3, 1918.

PREFACE TO FIRST EDITION

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 emphasise 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.

T. H. PEARMAIN.
C. G. MOOR.

September 30, 1895.

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MILK.

MILK may be defined as 'the fluid secreted by the lacteal glands of female mammals for the nourishment of their young.' In the case of cow's milk, it should be understood to refer to the whole milk of *healthy, properly-fed* cows.

The following table shows the composition of milk from different animals:

Kind of Milk.	*Water.*	*Fat.*	*Sugar.*	*Proteins.*	*Ash.*	*Analyst.*
Human ..	87·2	3·4	6·4	1·7	0·3	—
Cow ..	87·3	3·7	4·7	3·4	0·75	Richmond.
Goat ..	86·7	3·8	4·5	4·1	0·9	,,
Ewe ..	81·3	6·8	4·8	6·3	0·8	Vieth.
Ass ..	89·8	1·2	6·8	1·7	0·45	Richmond.
Sow ..	89·6	4·8	3·4	1·3	0·9	Vieth.
Mare ..	—	1·1	6·6	1·9	0·31	,,
Egyptian Buffalo	—	7·9	4·9	4·2	0·78	Pappel and Hogan.
Gamoose ..	84·2	5·5	5·4	3·8	1·0	Richmond.

The milk of sheep is largely used in the manufacture of Roquefort cheese. The milk of asses is much lower in fat and proteins than cow's milk; the casein is not readily curdled, on which account it is sometimes used as a substitute for human milk.

Mare's milk is alkaline in reaction, and the caseinogen behaves in a manner similar to that of human milk with acids and rennet. Koumiss, a preparation of mare's or ass's milk in a partly fermented condition, is largely used in Russia. It is prepared as follows: The milk is allowed to cool and deprived of a part of its cream; a little yeast is then added, which sets up a slow fermentation, the milk-sugar being converted into alcohol and lactic acid. Bell found Russian koumiss to have the following percentage composition: Lactic acid, 1·96; casein, 2·11; sugar, 0·40; fat, 1·10; alcohol, 2·12; ash, 0·34; water, 91·97.

Kephir, a preparation of cow's or goat's milk, very similar to koumiss, is produced by a special ferment. It is used largely by the tribes of the Caucasus.

The curdled milk of the buffalo, ewe, goat, and cow (youghourt), is largely used in Turkey. The milk is concentrated before inoculation with the ferment. A *Lancet* analysis showed 16·50 per cent. of total solids and an acidity equal to 1·3 per cent. of lactic acid.

Human Milk.—The composition of human milk is largely dependent upon the health and condition of life of the individual yielding it. The specific gravity varies from 1029 to 1035. Abnormal variations occur between the limits of 1017 and 1036. The proportion of sugar is very nearly constant, but the fat and proteins vary greatly in quantity, depending very much upon the stage of the nursing.

In the fat of human milk the volatile fatty acids are much lower, the fat globules generally smaller, and the melting-point of the fat lower than is the case with the fat of cow's milk.

On clotting, human casein is loose and flocculent, and is more easily digested by the child than cow casein, but the lower amounts both of casein and lime salts may be the factors responsible for this difference. Cow casein clots in large masses. Human milk is slightly richer in lactalbumin than cow's milk. By precipitin tests, it has been shown that both the casein and the albumin of human milk are biologically different to the analogous proteins of cow's milk.

The presence of lacto-globulins, also of different types as shown by the method of complement deviation, is thought to be certain. Human milk contains two or three times as much iron as cow's milk, but authorities do not agree on the respective quantities to be regarded as normal. Lane-Claypon, considering the later researches, regards 1·6 to 1·7 milligrammes of ferric oxide (Fe_2O_3) per litre as the figure for human milk, and adds that variation occurs in relation to the period of lactation. Infants absorb and retain a very much larger proportion of iron as it occurs in human milk than they do when the iron is derived from the milk of the lower animals.

Carter and Richmond think there to be another sugar as well as lactose in human milk, as gravimetric and polarimetric estimations, as used for cow's milk, both give very inaccurate results.

In the state in which it leaves the gland, human milk gives neither direct nor indirect reductase reactions and contains no proteolytic ferments. Peroxidases are sometimes found, but the occurrence of a lactase is doubtful. While a lipase is present, this appears to have no action on the milk-fat, and its presence has only been demonstrated after the addition of mono- and tri-butyrin. Enzymes acting on starch (amylase) and salol (salolase) and catalase are also present. Lane-Claypon ('Milk and its Hygienic Relations'), reviewing the work done on the enzymes in human milk, appears to regard none as possessing any useful action. In the absence of ferments reducing Schardinger's formalin-methylene blue reagent (absence of indirect reductases), and in the constant presence of salolase, human milk differs from that of cows.

Human milk, especially during the colostral period, contains important 'protective substances,' which, being transferred from the mother to the infant, increase the baby's resistance towards those diseases to which the mother is more or less immune. Though outside the scope of this book, this is mentioned here to further emphasise the vast inferiority that any artificial food has when compared with the natural food of the child.

As in cow's milk, two phosphatides (lecithin and cephalin) and nucleon are present.

The first portion of human milk to exude is poor in fat, the bulk of which comes in the end milk. An analysis of a particular fraction of the milk available at one time is of little value as far as the fat content is concerned; a specimen representative of the whole of a feed should be examined. Further, as the fat content varies to some extent, not with the time of the day, but with the relative period since previous feeding, it is well where fat is abnormal to examine specimens given at various times during the twenty-four hours.

There are a number of substances which, if taken by the mother, are known or supposed to pass into the milk. In most instances only minute amounts are excreted this way, though morphine, quinine, and potassium iodide are said to have been found in appreciable quantities. Alcohol taken by the mother may pass into her milk, but apparently only in negligible amounts; a finding similar to that of cows fed with brewer's grains. Administration of urotropine is likely to leave formaldehyde in the milk, though perhaps sometimes the drug is excreted unaltered. Arsenic, antimony, bismuth, zinc, mercury, and lead, have been found in human milk. There appears to be no evidence that the iron content (of cow's milk) is influenced by the administration of ferruginous drugs. When a mother is anæmic from loss of blood or constitutional causes, the iron content of the milk may be conspicuously low. Eric Pritchard says that in such cases the infant exhibits a number of symptoms of malnutrition associated with its anæmic condition.

The trace of boric acid sometimes to be found in human milk generally comes from a dusting powder. Bertrand and Agulhon certainly state human milk to contain 0·08 milligramme of boron per litre (cow's milk containing 0·2 milligramme), but such an amount would not be detected by ordinary methods.

The processes described for the analysis of cow's milk are available for the analysis of human milk, though the sugar is best estimated by difference.

Cow's Milk.

There being no definition having legal status of commercial milk in this country, we may point to that issued by the State of Queensland (1912) as being well worded: 'Milk shall be the normal, clean, and fresh secretion obtained by completely milking the udder of the healthy cow, properly fed and kept.' The Food Regulations, 1913, of Western Australia include the following clause: 'excluding that got during thirty days immediately before and five days immediately following parturition.'

Genuine milk is an opalescent white liquid, with a sweetish, bland taste. Milk contains water, fat, caseinogen, an albumin, milk-sugar, and salts, the latter consisting chiefly of the chlorides of potassium and sodium, together with the phosphates of potassium, calcium, and magnesium, citrates, and traces of sulphates. It contains two phosphatides (lecithin and cephalin), gases, and traces of urea, creatine, creatinine, orotic acid, and cholesterin, to some of which the characteristic flavour and smell of milk are due. The average composition is given in the table on p. 1. It is too voluminous and contains too little iron (Bunge) for the sole diet of adults.

The fat is suspended in the aqueous portion of the milk (milk plasma) in the form of globules, from 0·0015 to 0·01 millimetre in diameter. Small numbers of epithelial cells, leucocytes, and blood-corpuscles are frequently present, and in some cases colostrum. On standing for some time, a separation of part of the fat takes place, the larger fat globules of the milk naturally rising first.

Reaction.—Absolutely fresh milk is amphoteric in reaction—*i.e.*, blue litmus is turned red, and red litmus blue (due to the phosphates and citrates present); but usually by the time milk reaches the consumer it is faintly acid, owing to some slight production of lactic acid through bacterial fermentation of lactose. The rise in acidity is less rapid than increase of acid-forming organisms in milk (Revis and Payne).

When the fermentative change has resulted in the production of about 0·4 per cent. of lactic acid, the milk can be distinctly recognised by the taste to be sour. (The 'degrees of acidity' generally given in books denotes the number of cubic centimetres of decinormal alkali required to neutralise 100 c.c. of the milk.) Finally, when the acidity reaches 0·6 per cent., the milk curdles, spontaneously separating into a solid known as 'curd,' which consists of the fatty and protein constituents of the milk, and a clear liquid known as 'whey,' which is essentially a solution of milk-sugar and mineral salts. This change is also brought about artificially by the addition of rennet. The further changes which take place in the composition of the milk after curdling depend upon the nature of the bacteria which have gained access, various organisms giving rise to different fermentations.

Milk-Fat.—This is considered under 'Butter-Fat,' with which it is of course identical. Whether the fat globules consist entirely of fat or whether they are coated with protein is an open question. The identity in composition between the large and small globules is also a matter of doubt.

The growth-promoting 'vitamine' of milk is found in the butter-fat fraction (Stepp, also Osborne, Mendel, Ferry and Wakeman), and principally in the 'oil' fraction of the fat. No depreciation of growth-promoting efficiency occurs when butter-fat is heated with steam.

Milk also contains a scurvy 'vitamine' and a beri-beri 'vitamine,' but in what fraction these occur is not known. The rôle that milk plays in nutrition is still very imperfectly understood. Stepp found that mice soon died when fed on milk deprived of its lipoids (phosphatides), and the addition of butter-fat did not make up the deficient essential.

Milk-Proteins.—There are four proteins in milk—caseinogen (about 3 per cent.), an albumin called lactalbumin (about 0·4 to 0·5 per cent.), lacto-globulin, and a trace of Storch's mucoid. Caseinogen is not coagulable by heat, and belongs to the class of phospho-proteins. It occurs in milk as a calcium

and sodium salt combined with calcium phosphate. On the addition of rennet caseinogen is coagulated to form casein, the curdling being produced in two stages. The first is the action of the ferment 'rennin' upon the caseinogen to produce soluble casein, while the second stage is the action of the calcium salt, which precipitates the casein as curd, probably as calcium caseate. In the whey are the lactose, salts, and albumin, together with a new protein, called whey-protein, produced in the decomposition of the caseinogen. This whey-protein, being free from phosphorus, is incapable of conversion into casein. Caseinogen is also precipitated by dilute acids as free caseinogen. An instance of this has already been given in the description of the natural curdling due to the precipitation of the caseinogen by the formation of lactic acid. The lactalbumin is coagulated by heating to 70° to 75° C. This albumin is identical with that of the blood of the animal.

Milk-Sugar, or Lactose ($C_{12}H_{22}O_{11} + H_2O$).—This sugar is peculiar to the milk of the Mammalia. It is the most constant constituent of milk, from 5 to 6 per cent. being present in human milk, and 4 to 5 per cent. in the milk of most of the herbivora. Lactose has only a faint degree of sweetness, and is gritty when chewed. It is soluble in water, but insoluble in dry ether and in absolute alcohol. By slowly heating to 100° C. the molecule of water of crystallisation is driven off. Lactose is dextro-rotatory to a ray of polarised light, and reduces Fehling's solution. From the fact that polarimetric estimations of lactose show slightly higher figures than gravimetric estimations, Sebelien infers the presence of a pentose.

Milk-sugar is convertible by the action of dilute acids into galactose and glucose.

Citric acid, which readily inverts cane-sugar, has no action on lactose.

Saccharum lactis is an official preparation in the British Pharmacopœia, being used as a nutrient, and in the preparation of 'humanised milk' from cow's milk. The Pharmacopœia stipulates that it should not leave more than 0·25 per cent. of ash when

incinerated with free access of air, and that it shall indicate not more than 0·27 per cent. of hydrogen lactate (5 grammes in distilled water should not require more than 1·5 c.c. of decinormal sodium hydrate solution, using phenolphthalein as indicator). This standard is lenient, and a further test is desirable —that when boiled with fresh milk, the milk-sugar should cause no curdling.

Mineral Matter.—The mineral matter varies from 0·70 to 0·85 per cent.

According to König, the average composition of the ash of milk is as follows:

Potash as K_2O	24·0 per cent.
Soda as Na_2O	8·2 ,,
Lime as CaO	22·4 ,,
Magnesia as MgO	2·6 ,,
Phosphoric acid as P_2O_5 ..	26·3 ,,
Chlorine	13·9 ,,
Sulphuric acid as SO_3 ..	2·5 ,,
Iron	traces.

The iron content was found by Edelstein and von Cronka to vary between 0·4 and 0·7 milligramme of iron per litre (average 0·5 milligramme).

Variations in Composition.—The following are the chief circumstances on which the variations in the composition of cow's milk depend:

1. *The Breed of the Cow.*—Some breeds yield quantity, others quality. Heavy milkers, as a general rule, give lower percentages of fat and solids-not-fat than those yielding smaller quantities of milk. Guernsey and Jersey cows yield the most fat; shorthorns and red-polled cattle give the most milk. The average capacity of a cow's udder is about 5 pints, and the average annual yield about 420 gallons.

2. *The Time and Stage of Milking.*—Cows are usually milked twice a day, the morning milk as a rule being the larger in quantity and poorer in fat, because of unequal length of time between milking. The milk which is first drawn—the 'fore milk'—contains very much less fat than that last drawn—the 'strippings.' This is due to a partial creaming

taking place in the udders. Dishonest dealers take advantage of this fact in adulteration cases, by having the cows partially milked in the presence of ignorant witnesses, so that the resulting milk consists largely of the 'fore milk.'

3. *The Age of the Cow.*—Young cows give less milk, cows from four to seven years old give the richest milk, and less milk is given with the first calf. Cows usually become milkers in the third year. They give the largest yield, according to Fleischmann, after the fifth until the seventh calf. After the fourteenth calf they yield, as a rule, no more milk.

4. *The Time of the Year.*—Richmond divides the year into four periods, according to the character of the milk yielded: (1) November, December, and January, the milk is rich in fat and solids-not-fat; (2) February, March, and April, the fat figure drops, while the solids-not-fat remain practically the same; (3) May, June, July, and August, the fat is low, but rises towards the end of the period. In May and June, when the cows are removed from the byres to the fields, the fat sometimes falls slightly below the standard of the Board of Agriculture, in the case of the morning milk,* but only rarely in the case of the evening milk. In July and August the solids-not-fat fall, sometimes even below 8·5 per cent. In the last period (September and October) both fat and solids-not-fat improve in quantity.

While the content of milk-sugar remains nearly constant throughout the year, the percentage of proteins tends to be higher in autumn and spring than in winter and summer (H. C. Sherman).

During a period of drought there is a tendency for the fat to increase, and the solids-not-fat to decrease in quantity. This does not always happen, for Liversedge, after comparing the rainfall in

* The low fat figures, previously only of significance in confusion with adulteration in May and June, commenced in 1914 in February and continued till August, though May and June were the worst. The year 1914 was exceptional, and the poor morning milks were fewer in 1915 and 1916, and only existed during April to July (Arup, Huish, and Droop Richmond).

August and September for the ten years 1902 to 1911 with the composition of the milk samples examined during the same months, found 1903, which had the highest rainfall (5·2 inches), and 1911, which had nearly the lowest rainfall (1·4 inches), gave the same average composition.

5. *The Mental and Physical Conditions under which the Animal is kept.*—If the cows are worried or driven about, the quantity and yield of the milk are reduced. If they are kept warm and well fed, the quantity and quality of the milk are naturally increased.

6. *The Food.*—The natural food, fresh grass, is the best, hay being the next most suitable food. The greater the proportion of the nitrogen in the food, the greater the yield of the milk, the proportion of fat being especially high. Beets, carrots, and swedes increase the proportion of milk-sugar. Feeding with brewers' grains depreciates the quality by lowering the total solids of the milk. This objectionable practice has been made illegal in the State of Wisconsin, U.S.A. Cows overfed on cake are said to give as poor a milk as when underfed. The New York Expt. Station (1904) found that the composition of milk bore no definite relation to amount or kind of food taken, and that cows fed for three months on fat-free food gave milk similar to that given when fed on food containing fat.

The administration of salt does not necessarily result in the excessive consumption of water, and, in any case, the amount drunk appears to have no direct influence on the composition of the milk.

When animals receive too small a quantity of food, the milk tends rather to decrease in amount than to show abnormal comparative proportions of its constituents.

7. *The Period of Lactation.*—The results of various researches destined to show the effect of this factor require some reconciliation. The difference in periods elapsing between parturition and next pregnancy in particular prevents any useful co-ordination of the different sets of experiments.

8. *The Soil.*—Richmond (*Analyst*, 1904, p. 181) thinks that milk raised on cretaceous formations tends

to be better in quality than that from New Red Sandstone and Oxford Clay.

9. *The Health of the Animal.*—The cow is liable to certain diseases which affect man, and some of these may be conveyed by the ingestion of milk containing specific pathogenic bacteria. Cow's milk containing bovine tubercle bacilli is clearly a cause of tuberculosis in man. Various figures (varying from 2 to 25 per cent.) are given to show the amount of milk containing the tubercle bacillus. Outbreaks of sore throat in man have been attributed to the milk of cows suffering from mastitis, and diarrhœa is sometimes due to the ingestion of milk from cows affected with enteritis. It is known that milk from cows suffering from foot and mouth disease may produce, especially in children, an illness attended with aphthous stomatitis, swelling of the tongue, and fœtor of the breath, or, on some occasions, severe tonsillitis.

While diphtheria is sometimes spread by milk, it can generally be discovered to be of human contamination, and not of bovine origin. Doubt exists if scarlet fever can be ever attributed to illness in a cow. (See monograph on 'The Bacteriology of Milk' in 'Aids to Bacteriology' for further information on the rôle of milk in conveyance of disease.)

Hewlett, Revis, and Villar, have noticed an abnormally low content of lactose in milks containing a high cell content. On two occasions we have found that milk containing abnormally low amounts of ash contained pus. On the contrary, Seel mentions a rise in the ash of milk from cows with mastitis. Speaking generally, illness of a cow more frequently affects the quantity of milk than its percentage composition.

Milk is subject to certain diseases peculiar to itself of a bacterial nature—ropy milk, bitter milk, soapy milk, blue milk, red milk, and yellow milk. (See 'Applied Bacteriology,' Moor and Hewlett. Baillière, Tindall and Cox.)

Milk when obtained from healthy and properly-fed cows is fairly constant in its composition. For many years Droop Richmond communicated to the

Society of Public Analysts an annual paper on the composition of milk based on the analysis of an enormous number of samples—these are to be found in the *Analyst*. Although the yearly differences are not great, genuine milk does appreciably fluctuate in composition. From 1882 there was a gradual fall in the fat figure till 1892; for two or three years the quantity of fat remained about the same, then came a fall, until the Sale of Food and Drugs Act of 1899 came into force, when the percentage of fat began to rise. In 1909 a fall set in again, which continued to 1913, and then a rise started. This rise has been progressive through 1914, 1915, 1916, to drop in 1917. These fluctuations cannot be directly attributed to specific causes. In some years climatic conditions may be the cause, and the rise in 1899 was attributed by Richmond to the fact that the farmers' attention had been called to the necessity for quality as well as quantity. It is probable that the last fall was due to farmers keeping 'heavy milkers,' and weeding out those giving small amounts of milk.

H. D. Richmond, Huish, and Arup (*Analyst*, 1917, p. 119) give the average composition of 49,721 samples of milk received from farms during 1914, 1915, and 1916:

	Morning Milk.	*Evening Milk.*	*Average.*
Specific gravity	1·0319	1·0317	1·0318
Total solids	12·49	12·71	12·60
Fat	3·65	3·87	3·76
Solids-not-fat	8·84	8·84	8·84

The same authors (*ibid.*) give a table showing the incidence of low fat figures in morning milk in April, May, June, and July, 1915:

Percentage of Fat.	*Percentage of Samples.*			
	April.	*May.*	*June.*	*July.*
2·9 to 3·0	0·8	0·9	2·5	1·2
2·8 „ 2·9	0·4	0·4	0·8	0·7
2·7 „ 2·8	0·2	0·1	0·3	0·1
Below 2·7	—	—	—	0·3

Though individual cows may give milks that in either the fat or solids-not-fat figures may fall below the standard adopted by the Board of Agriculture, such deficiencies very rarely occur when the mixed milk of a herd is taken.

When a milk is naturally deficient in solids-not-fat, this is very often due to a deficiency of milk-sugar. Less frequently, the protein figure may drop while the lactose remains normal. In either case there is generally a normal figure for the ash.

Arnaud has shown that in very cold weather the ice formed in milk contains a little fat and milk-solids. The portion that remains unfrozen, however, contains a higher proportion of both fat and solids-not-fat than the original milk.

Milk Standards.—Section 4 of the Sale of Food and Drugs Act, 1899, conferred upon the Board of Agriculture power to 'make regulations for determining what deficiency in any of the normal constituents of genuine milk, cream, butter, or cheese, or what addition of extraneous matter or proportion of water, in any sample of milk (including condensed milk), cream, butter, or cheese, shall for the purposes of the Sale of Food and Drugs Acts raise a presumption, until the contrary is proved, that the milk, cream, butter, or cheese, is not genuine or is injurious to health, and an analyst shall have regard to such regulations in certifying the result of an analysis under those Acts.' In pursuance of these powers, the Board of Agriculture made the following regulations, which are cited as the Sale of Milk Regulations, 1901:

Milk.—'Where a sample of milk (not being milk sold as skimmed, or separated, or condensed milk) contains less than 3 per cent. of milk-fat, it shall be presumed for the purposes of the Sale of Food and Drugs Acts, 1875 to 1899, until the contrary is proved, that the milk is not genuine, by reason of the abstraction therefrom of milk-fat, or the addition thereto of water.

'Where a sample of milk (not being sold as skimmed, or separated, or condensed milk) contains less than 8·5 per cent. of milk-solids other than milk-

fat, it shall be presumed, for the purposes of the Sale of Food and Drugs Acts, 1875 to 1899, until the contrary is proved, that the milk is not genuine by reason of the abstraction therefrom of milk-solids other than milk-fat, or the addition thereto of water.'

Regulation 3 of the above Regulations, which dealt with skimmed or separated milk, is revoked and replaced by the Sale of Milk Regulations, 1912, which states:

'Where a sample of skimmed or separated milk (not being condensed milk) contains less than 8·7 per cent. of milk-solids other than milk-fat, it shall be presumed for the purposes of the Sale of Food and Drugs Acts, 1875 to 1907, until the contrary is proved, that the milk is not genuine, by reason of either the addition thereto of water, or the abstraction therefrom of milk-solids other than milk-fat.'

In cases where the milk falls below the standard, the onus of proof that the milk is genuine falls on the vendor. The Board suggests that in the absence of any special circumstances indicating that the case is a fraudulent one, the Local Authority may call the vendor's attention to the analyst's report, and inquire whether he desires to offer any explanation, and if they are able to accept the explanation, they may refrain from further proceedings.

At the time of writing, provided deficiency is due, not to actual sophistication of the milk itself, but to the production of impoverished milk by cows, then the sale is not to the prejudice of the purchaser. Three justices against two, in Hunt *v.* Richardson, in effect decided that, even where a farmer has fed cows to secure a maximum yield irrespective of its quality, the product is milk. In Grigg *v.* Smith, the milk which contained only 2·6 per cent. of fat was obtained by the partial milking of a cow, some being left in her for the calf. Nothing having been added to or abstracted from the milk, the King's Bench held there to be no offence on its sale. Mr. Justice Atkin added that a farmer was now entitled by law to give a preference to his own calves over the babies of his customers. The Bench unanimously agreed that the present position required reconsideration.

There is little doubt that in some quarters an extensive amount of 'watering down' with water or skimmed milk takes place. This is a profitable proceeding, since 30 per cent. of skimmed milk can be added to an ordinary good milk without bringing the fat figure below 3 per cent. Such 'toning' is actually sanctioned in British Honduras under Ordinance of 1914, if the resulting liquid is not reduced in strength to below the exceptionally low standards required in that colony.

Milk may also be impoverished by keeping back and leaving out of bulk the 'strippings' (*i.e.*, the last drawn and richest portion). A low solids-not-fat figure may be due to an excess of fat. The addition of cream to milk has much the same effect in reducing the solids-not-fat figure as has the addition of a similar bulk of water. It becomes a matter of a simple calculation to ascertain whether or no the excess of fat justifies an opinion that this alone will explain the deficiency.

The 3 per cent. standard for fat is in use in many other countries, but only 2·8 per cent. is required in British Honduras (1914). New Zealand (1909) and British Guiana (1913) require 3·25 per cent., and Western Australia 3·2 per cent. (1913).

While 8·5 per cent. of solids-not-fat is accepted in many countries as a fair standard, British Honduras (1914) only requires 8·0 per cent.

Next to actual watering, partial skimming of whole milk, or, what amounts to the same thing, the addition of separated milk to whole milk, constitutes the most frequent form of adulteration of milk.

Every 10 per cent. of the fat removed from whole milk represents approximately the loss of half an ounce of cream from the quart of milk, the value of which is about a penny, thus proving a very profitable adulteration to the dishonest vendor.

By means of an emulsifying apparatus, skim milk is sometimes mixed with fats other than butter-fat, and the resulting product is sold as whole milk.

Skimmed and Separated Milk.—Hand-skimmed milk has now practically disappeared from commerce

Cream is now separated from milk by centrifugal separators, the best forms of which do not leave much more than 0·1 per cent., or at most 0·2 per cent., of fat in the separated milk. The solids-not-fat are, owing to the removal of the fat, proportionally higher than in whole milk.

The present standard of 8·7 per cent. of non-fatty solids (*vide supra*) was originally suggested by Colonel Cassal in 1910. Both Western Australia (1914) and Natal (1914) require 8·8 per cent. It can only be sold in the Federated Malay States (1916) if it bears a label stating that it must not be given to sick people or children.

The Analysis of Milk.

Sampling.—When milk is sampled, the whole quantity contained in the vessel should be stirred up, so as to insure a complete distribution of the cream throughout the body of the milk. If a sample is to be divided into three parts, one pint should be purchased and poured into bottles of such a size as to be filled almost, but not quite, to the cork. If they are filled entirely, it is difficult to shake them so as to mix in the cream; while if they are not filled up to the neck, the shaking of the milk in transit may cause some of the cream to be churned into butter.

We now describe in detail the methods of analysis ordinarily applied to milk:

Specific Gravity.—The specific gravity may be taken either by a delicate hydrometer or (more exactly) by a Westphal balance.

The term 'Recknagel's phenomenon' is applied to the increase observed in the specific gravity of milk, which takes place some time after milking. Droop Richmond (*Analyst*, 1894, p. 76) gives an example of this, the results of which were as follows:

Specific gravity	1½	hours	after milking..	1031·0
,,	3½	,,	,, ,, ..	1032·2
,,	18	,,	,, ,, ..	1032·5

This rise in the specific gravity must not be confounded with a similar rise when frothy milk is allowed to stand.

The samples should be shaken gently just before taking the gravity, so as to mix in the cream, but avoiding the creation of air-bubbles. The specific gravity of genuine milk generally falls between 1029 and 1034 at 15·5° C. If the gravity be taken at another temperature, it can be corrected for temperature by means of a table. It is, however, a simple matter to stand the samples in water at the required temperature, until they attain this temperature.

Milk samples should be examined at the earliest opportunity, as when curdling has commenced the estimation of the gravity is impossible.

It is generally inadvisable to add ammonia to sour milk for the purpose of removing thickness. Determinations of total solids on the ammoniacal milk are certain to be below the truth and erratic as well, while, except when estimated by the Gottlieb process, the fat estimations will also be low.

A satisfactory mixture of a curdled milk can be made by turning the whole of the sample into a beaker and 'whipping' with an egg-whisk. The specific gravity of a sample after it has been treated in this way is not accurate. 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 an adulterated sample may possess the same gravity as that of genuine milk. Whether, therefore, the specific gravity is normal or otherwise it is necessary to estimate the fat and total solids.

The Freezing-Point.—The freezing-point of milk is subject only to faint variation in genuine samples. It appears to be independent of variations in the amounts of lactose, proteins, and fat, and to depend on the soluble salts. The results are only accurate when the milk is fresh, or at any rate is not sufficiently sour for this to be tasted or smelt. Lactic acid increases the freezing-point depression (Δ)—*i.e.*, lowers the freezing-point. While Stoecklin (abstract, *Analyst*, 1911, p. 345) has suggested a

correction for lactic acid, Monier-Williams regards it with suspicion. The freezing-point is raised by the addition of water to milk, but the various authors who have dealt with the subject are not in strict agreement as to the normal milk figure. Stoecklin considers a freezing-point above $-0{\cdot}530°$ to be conclusive evidence of watering, and accepts a normal freezing-point of $-0{\cdot}550°$ as proof of genuineness whatever be the results of chemical analysis.

Henderson and Meston give the normal variation as from $-0{\cdot}55°$ to $-0{\cdot}56°$ C., and mention a rise of $0{\cdot}005°$ as indicating the presence of about 1 per cent. of water. The Dutch *Codex Alimentarius* assumes the presence of added water if the freezing-point is above $-0{\cdot}54°$ C. Van der Laan takes a figure exceeding $-0{\cdot}53°$ C. as evidence of adulteration. Monier-Williams found values ranging from $-0{\cdot}558°$ to $-0{\cdot}514°$ C. Reliable results are only to be obtained by recognition and avoidance of many sources of error, for details of which, as well as for a description of a cryoscopical apparatus, reference should be made to a Report to the Local Government Board by Dr. Monier-Williams (Food Reports, No. 22, 1914).

An abnormally high content of sodium chloride is sometimes found in milk which, though low in its content of solids-not-fat, is genuine. To its presence can be attributed the possession of a normal freezing-point. Henderson and Meston explain the cause: the mammary glands of the cow, when unable to obtain the correct proportion of food-stuffs, adjust the osmotic pressure by adding an extra proportion of common salt from the blood.

Total Solids.—A shallow platinum or porcelain dish is ignited and weighed, about 5 grammes of the milk are added, and the dish and milk are quickly weighed again. The difference will be the weight of milk taken. Delay in weighing will result in the evaporation of a little water. The dish is placed on a water-bath until all the water has apparently been driven off, when it is placed inside a water-oven for three or four hours. At the end of this time the dish is allowed to cool in a desiccator and weighed. It is then replaced in the oven for an hour, allowed to

cool, and weighed again. This hourly heating and weighing is repeated until the difference between two consecutive weighings does not exceed a milligramme. The difference between the final weight and the weight of the dish will be the total solids, and this divided by the amount in grammes taken and multiplied by 100 will be the percentage of total solids.

To prevent the formation of a 'skin,' which consists of coagulated casein and lime salts, on the surface of the milk during evaporation, some analysts add a few drops of a 10 per cent. acetic acid in alcohol solution, or acetone. There is difference of opinion whether such addition interferes with the accuracy of the figure or not, our own experience being that the inaccuracy is too small to be of any consequence. The skin may be broken from time to time with a mounted needle or thin platinum wire.

The temperature inside the water-oven should really reach 100° C.; some water-ovens give a much lower temperature.

The milk-solids should be weighed at once after drying, as they absorb moisture from the air very readily; moreover, as is well known, an increase of weight takes place with all platinum articles on cooling, due to the occlusion of gases on their surface.

When the milk is sour, part of the lactic acid will be volatilised unless a fixed alkali is added. The milk is weighed in a dish as before, and a drop of phenolphthalein solution is added. Decinormal solution of caustic soda is then added until the free acid is neutralised. A note is made of the amount of caustic soda solution added and 0·0022 gramme is deducted from the weight of total solids for each cubic centimetre of decinormal sodium hydrate added. (From the weight of ash obtained on a sample so treated 0·0053 gramme is deducted for each cubic centimetre of decinormal soda added. An ash figure so determined is, however, not always accurate. A correct figure is obtained on a sour milk, when the ash is determined in the usual way.) In the Government Laboratory decinormal strontia is used instead of caustic soda, and in the case of this alkali 0·00428 gramme is deducted from the

weight of total solids for each cubic centimetre of decinormal strontia added.

The total solids of genuine milk rarely fall below 12·2 per cent. In them the lactose is probably in the anhydrous state. When dried to constant weight, the weight of the solids is slightly below the sum of the weights of the constituents. Splittgerber attributes this to the action of lactic acid, especially on casein and lactose.

The constituent of milk most affected by keeping is lactose, which gives rise, directly or indirectly, to a variety of products—lactic acid, ethyl alcohol, and acetic acid being the principal ones. Over 100 varieties of micro-organisms are capable of converting the lactose into dextrose and galactose, and the galactose into lactic acid. Butyric acid is sometimes produced, but the quantity is apparently very small, as a rule. It is generally supposed to be derived from lactic acid, but this is disputed by Richmond. Acetic acid may be produced by the oxidation of lactic acid, or of the ethyl alcohol which is invariably present in sour milk. Ethyl alcohol is produced by the fermentation of lactose and galactose by certain schizomycetes. Small amounts of higher alcohols, succinic acid, and glycerol are also sometimes to be found, but their amounts are small enough to be negligible. By the alteration of the proteins small amounts of ammonia and amino compounds are also formed. Reference is made to the existence and estimation of these compounds in the monograph on the Maceration Process (p. 23).

Estimation of the Ash.—The dish containing the total solids is heated cautiously at a temperature as low as possible over a Bunsen or Argand burner, or in a muffle furnace heated to a dull red heat, until a white ash is left. In the process of ashing, portions containing unburnt carbon will sometimes stand away from the surface of the dish. These should be broken down by touching with a platinum wire. Overheating will cause loss of sodium chloride. The ash of normal milk is about 0·73 per cent., and is slightly alkaline. If the ash is found to be materially less than this, it would point to watering.

The ash does not represent the whole of the content of mineral matter of the sample. Sulphates are pretty certain to be low, the organic phosphorus may appear in different combinations in the ash, and a little chlorine is likely to be lost.

Estimation of the Fat.—The different methods of determining the fat may be classified as follows:

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

2. By simple extraction, with a solvent, of the dried milk.

3. By extraction of the fat with a solvent after destruction of the casein by acid or solution of the casein in ammoniacal alcohol.

Mechanical Methods.—The Leffmann-Beam and the Gerber methods depend on the liberation of the fat from the milk by treatment with sulphuric acid. The application of centrifugal force then causes the fat to rise up into the neck, which is graduated.

Leffmann-Beam Process.—Small flat-bottomed flasks are supplied for use with this machine, graduated on the neck into eighty divisions, ten of these divisions corresponding to 1 per cent. of fat by weight on 15 c.c. of milk.

The procedure is as follows: 15 c.c. of milk are run into the bottle, 3 c.c. of a mixture of equal parts of amyl alcohol and hydrochloric acid added, the bottle well shaken, and then 9 c.c. of sulphuric acid (commercial), which is added slowly with agitation. This fills the bottle to within 3 or 4 c.c. 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 centrifuged 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 containing duplicate estimations 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.

A cloudy layer between the fat and the acid liquid 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 0·4 per cent. in excess of the truth.

Fusel oil assists the collection of the fat globules, but does not itself cause any increase in the fat column, as it dissolves in the acid liquid.

The bottles are not always accurately graduated, and each should be standardised by comparison with results obtained by one of the accurate methods.

Gerber Process.—The Gerber apparatus consists of a hollow disc about 18 inches in diameter, on which are clips for holding the test-bottles or acidobutyrometers; these, when placed in position, are covered by a plate that fits over the disc, forming a hollow box. The disc and its contents are rotated by giving fifteen to twenty sharp pulls with a strap, and the apparatus will run by itself for the three minutes which suffice to separate the fat completely. The procedure is as follows: 10 c.c. of sulphuric acid, from 1·820 to 1·825 specific gravity, are placed in the bottle; then 11 c.c. of the milk to be tested is run down the side of the bottle, so that it does not mix with the acid at this stage. Finally 1 c.c. of amyl alcohol is run down the side of the bottle. At this stage, the three liquids should form three distinct layers. The bottle is closed with the indiarubber stopper, and shaken till the ingredients are mixed, and the solution changes to a dark brown. It is then rotated in the machine for three minutes, put

in a bath of water at 60° C. for a minute, and then the reading of fat taken. If the top of the fat column does not precisely correspond to one of the graduations, it is readily made to do so by moving the indiarubber stopper slightly, with care so that no fat jumps up into the conical bulb. The reading is taken from the bottom of the fat meniscus to level line at the bottom of the fat column.

When separated milk is used, the milk must be shaken for two to three minutes, and, after rotating, the test-bottle is to be placed in hot water for a few minutes; this rotating and warming is to be repeated three separate times.

The Maceration Method.—This process, originally devised by Bell, is applicable to sour milk, and is used by the referees under the Sale of Food and Drugs Acts in the Government Laboratory. Two important papers on the process, one by Thorpe, the other by Richmond and Miller, are to be found in the *Analyst*, 1905, p. 197, and 1906, p. 317, respectively. We are indebted to these papers for the details and criticisms of the technique of the process. As the fat and the solids-not-fat are estimated on the same portion of milk, the following description includes both estimations, and, for convenience, the methods for determining the allowance for decomposition are also given here. The latter portion of the investigation includes corrections for the alcohol formed, the volatile acids, and the corrections for protein change, these being the determinations performed in the Government Laboratory.

The following description of the process is that given by Thorpe (*loc. cit.*) while the comments are chiefly made by Richmond and Miller (*loc. cit.*). The contents of the sample bottle are transferred to a suitable vessel and thoroughly mixed with a wire whisk. On one portion a direct estimation of the total solids is made, while duplicate portions of the sample, each about 10 grammes in weight, are weighed out into flat-bottomed platinum (or aluminium) basins, each of which has been tared along with a short glass rod having a flattened end. Two drops of a 0·5 per cent. solution of phenolphthalein

are added, decinormal strontia is run in to each of the weighed duplicates till alkaline, and the measure of strontia solution noted. The milk is then evaporated over the water-bath until the residue, which towards the end should be dried at a very gentle heat on a hot plate and with constant stirring, attains the consistency of dry cheese. The basin is removed from the water-bath or hot plate. About 20 c.c. of dehydrated ether are next poured over the milk solids, which are then carefully triturated with the glass rod. The ethereal solution of the fat is then decanted through a filter (diameter 9 centimetres), which has been previously dried and weighed in a weighing bottle. A further treatment with ether is performed, and after the ether has cleared it is passed through the filter. The solids are ground to a very fine powder, and subjected to some seven or eight successive treatments with ether (Richmond says that this is not sufficient, and that twenty or thirty treatments are necessary). Before becoming quite dry the solids are transferred as far as practicable to the weighing bottle; the filter-paper, washed free from fat, is replaced in the bottle, and the whole, with the platinum basin containing the small adherent quantity of solids, is dried at 100° C. for three hours and then weighed. The weight is again taken after drying for a further two hours, and a final confirmatory weighing after another hour. The last two weights should not differ by more than a milligramme. Deducting 0·00428 gramme for each cubic centimetre of decinormal strontia used in the neutralisation, the result gives the amount of non-fatty solids present in the quantity of milk operated on. The ether is distilled off from the ethereal solution, which has been received in small tared flasks, and the residual fat weighed. If desired, the phenolphthalein, being insoluble in petroleum ether, can be separated, but the error due to this is small enough to be negligible.

The average difference between the figures for solids-not-fat, obtained on fresh milk by the Maceration and the S.P.A. methods, is given by Richmond as 0·20 per cent., the former process giving the higher

figure. This observer partly attributes the difference (*loc. cit.*) to a portion of the milk-sugar in the solids-not-fat obtained by the maceration process being in the hydrated condition, which makes an increase of about 0·1 per cent., while some of the milk-sugar in sour milk may be converted into hexoses, which also gives a higher figure. Further, an error, in the direction of an increase, is shown by Richmond to be caused by the inevitable presence of aldehyde in the ether which is absorbed by the solids, probably by a condensation of the COH group with the free amino groups of the proteins. It is probable that the browning of the solids obtained in the Society of Public Analysts' method is due to decomposition, with the formation of formic acid before all the water has been expelled, and may account for the remainder of the difference between the two methods. The fact that slightly higher figures are obtained when the milk is spread over a large surface, and a browning of the solids thus avoided, seems to support this contention. It is stated that the fat in sour milk varies from 0·06 per cent. more to 0·15 per cent. less than in the fresh milk, the average being 0·05 per cent. less.

The Alcohol Correction.—The alcohol is determined in the Government Laboratory in the following way: 50, 75, or 100 grammes of the milk are distilled, and the distillate neutralised with decinormal caustic soda, litmus paper being used as the indicator. The neutralised distillate is then redistilled, the distillate made up to a convenient bulk, and the specific gravity taken by means of a 50-gramme pycnometer. The alcohol is deduced from a table. The percentage by weight of alcohol, multiplied by $\frac{20}{46}$, gives the percentage of lactose that has disappeared in the production of the alcohol.

The Volatile Acid Correction.—Ten grammes of the milk are weighed in a platinum capsule and neutralised to the extent of one-half the total acidity (the total acidity having previously been determined on another portion) by means of decinormal caustic soda, and a little phenolphthalein is added. The mixture is evaporated to dryness on a water-bath

with frequent stirring, and then 20 c.c. of boiling distilled water are added to thoroughly detach the milk-solids from the capsule. A further addition of decinormal soda is made until the milk is neutral. The difference between the original acidity and that obtained on the evaporated portion is regarded as acetic acid. The production of 60 parts of acetic acid denotes a loss of 62 parts of the original lactose. It is seldom necessary to take the formation of butyric acid into account, but the details will be found in the papers by Thorpe and Richmond (*q.v.*). Richmond finds that this volatile acid correction fails in the following particulars: There is always carbonic acid present, which would be driven off and thus calculated as acetic acid; all the volatile acids are not driven off; and there is also a possibility of lactic acid being volatile, and this acid may be partly converted into a lactone. Richmond gives a modified method for calculating the results (*Analyst*, 1906, p. 324).

The Ammonia Correction.—Two grammes of the milk are made up to a volume of 100 c.c. with ammonia-free distilled water, and filtered through a carefully washed filter. In 10 c.c. of the clear filtrate, increased to 50 c.c. by the addition of ammonia-free distilled water, the ammonia is determined by means of Nessler's method, using a standard solution of ammonia containing 0·01 milligramme of ammonia per c.c. Richmond has shown very good reasons for questioning the validity of the ammonia correction, but as it is usually so small he accepted it.

Tillmans, Splittgerber, and Riffart have shown that milk fresh from the cow contains from 3 to 4 milligrammes of ammonia per litre, and are of opinion that any milk having more than 10 milligrammes per litre cannot be considered to be fresh milk.

Adams' Method.—Five c.c. of the milk are spotted by means of a pipette on to an Adams paper, which is allowed to dry, and is then rolled up. The weight of this 5 c.c. of milk is ascertained by pipetting a similar amount into a tared dish and weighing it. After the paper has dried in the air in a place free

from flies, it is placed in the water-oven for a few minutes' final drying, and extracted in a Soxhlet extractor. A handy form of condenser is the hollow metal ball, which is more efficient than a 3-foot tube condenser. The fat flask should have a short wide neck. Sufficient ether (specific gravity 0·720) should be used to fill the Soxhlet one and a half times, and it should be extracted for about four hours. A light screw of paper in the top of the condenser tube limits 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. It is scarcely neessary to observe that the flask should on no account be heated over a naked flame, but in a vessel containing water at about 60° C., the flask being partially immersed in the water and the ether kept in a state of gentle ebullition. When the extraction of fat is complete, the ether is distilled off from the fat in the flask, and the latter placed in a water-oven to complete the drying.

A very slight error is introduced into this process by the passage of fibres from the coil into the flask. To remove this source of error, Revis has designed a strainer composed of bass, which is put into the Soxhlet extractor below the coil, and thus prevents the passage of fibres. The error due to this cause is, however, sufficiently small to be disregarded for most purposes.

Petroleum ether or carbon bisulphide may be used for extracting instead of ether.

Werner-Schmid Method.—This method was first introduced into this country by A. W. Stokes. Ten grammes of the milk are weighed into a Stokes tube, and 10 c.c. of strong hydrochloric acid are added. The tube is then heated over a flame with constant

shaking until the contents turn a dark brown, owing to the action of the acid on the lactose. On allowing to stand, the fat will be seen to collect on the surface in a clear layer. The tube is now cooled by immersion in water, and then about 30 c.c. of dry ether are added. The tube is corked, well shaken, and placed aside until the ether layer is quite clear. As much as possible of this ether layer is removed into a tared flask (preferably by means of wash-bottle tubes), and a further amount of 20 c.c. of ether is added, the tube again shaken well, and the ether removed into the flask when clear. The extraction with 20 c.c. of ether is repeated twice more, making in all four extractions. The ether is now distilled off from the flask and the residue of fat weighed, after being dried in the water-oven. Ether extracts a very small amount of substances other than fat from the acid liquid. It is therefore desirable, after the flask has been dried and weighed, to extract the fat with petroleum ether, which leaves the other ether-soluble substances. The flask with the matter insoluble in petroleum ether is then weighed, and the weight of the latter subtracted from the weight of fat. In the process described above the whole of the fat is extracted. It was formerly the practice to add one quantity of 50 c.c. of ether, to pipette off an aliquot part, weigh the fat obtained from this quantity, and calculate the amount in the total volume of ether remaining after shaking. This process gives a result close to those obtained by the Adams, Maceration, and Centrifugal methods. With sour milks it tends to give high results, owing to the slight solubility of lactic acid in ether.

Gottlieb's Method.—About 5 grammes of milk are weighed into a narrow, stoppered cylinder holding about 50 c.c. 0·5 c.c. of ammonia solution (0·88 ammonia diluted with an equal bulk of water) is measured in; and well mixed with the milk. Five c.c. of 95 per cent. alcohol are added (methylated spirit, if free from petroleum, will serve), and the mixture shaken till homogeneous. 12·5 c.c. (*circa*) of ether (methylated, specific gravity 0·720, preferably freshly distilled, to remove the acrid substance formed on

standing) are poured in, and the contents of the tube well mixed, the thorough mixing at this stage being, perhaps, the most important detail. Finally, 12·5 c.c. of petroleum ether (boiling-point below 60° C.) are added, and the contents of the tube again thoroughly mixed two or three times; separation of the ethereal layer takes place rapidly, and when globules can no longer be detected in the lower layer, the upper layer is drawn off with wash-bottle tubes; by the addition of successive quantities of a mixture of ether and petroleum ether (the recovered solvent serves admirably) the whole of the fat is extracted. The solvent is removed by distillation and the fat dried and weighed. The fat is dissolved in petroleum ether, and the solution decanted from the minute residue, and after three or four washings with petroleum ether the residue is dried and weighed. If desired, the quantities given may be doubled, or increased in any other ratio, provided that the relative proportions are strictly adhered to.

This process is most reliable, but as some people find it to give erratic figures in their hands, its results should only be accepted when, by careful comparison with those obtained by other methods, the worker feels full confidence in them.

Error may arise through addition of the various substances in the wrong order, through failure to obtain a proper mixture after each addition, or through the use of petroleum ether that is not completely volatile at the temperature of the water-bath.

The process works admirably—better, in fact, than any other—with sour milk. But in this case the mixture of ammonia and milk must be thorough, so as to produce a perfectly homogeneous fluid. If necessary, more ammonia may be added to attain this. Failure in this respect leaves small particles of coagulated casein which effectively protect any fat occluded in them from the action of the solvents, and a low result is obtained.

Calculation Method.—A relation between the gravity, fat, and total solids, enables us to calculate the third factor, if the other two are known.

Extended tables for the Hehner-Richmond formula

are published (*Analyst*, vol. xiii., p. 26). A more ready method of applying the formula is by the instrument described below.

Richmond's Milk Scale.—This rule has three scales: two for total solids and fat respectively are marked on the body of the rule, while that for specific gravity is placed on the sliding part. The divisions are as follows: Total solids, 1 inch divided into tenths; fat, 1·164 inches divided into tenths; specific gravity, each division = 0·254 inch. These numbers show the relation according to the formula

$$T = 0{\cdot}25\,G + 1{\cdot}2\,F + 0{\cdot}14.$$

Example: A sample has a specific gravity of 1032, and 3·5 per cent. of fat. The sliding portion of the rule is adjusted so that the arrow points to 3·5 per cent. of fat. The figure representing total solids will now be exactly below the gravity figure (32), and in this particular case will show the total solids to be 12·35 per cent.

On another part of the rule will be found a scale for correcting the specific gravity to 60° F., when it has been taken at some other temperature. This is done by placing the arrow at the 60° F. mark on the scale of temperature on the slide against the degrees of specific gravity found, when the temperature at which the gravity was taken is found against the gravity corrected to 60° F. It is seldom that the total solids calculated in this way deviate from those found by actual determination by more than 0·2 per cent.

The Calculation of Amounts of Added Water and of Skimming.—Should the solids-not-fat be less than 8·5 per cent., the milk has been adulterated by the addition of water, and the amount of water added is found by subtracting the solids-not-fat figure from 8·5, multiplying by 100 and dividing by 8·5. This will give the parts of added water in a hundred parts of the milk.

Should the solids-not-fat figure be not less than 8·5, and the fat figure be less than 3 per cent., the milk has been adulterated by the abstraction of fat (or by

the addition of skim milk, which amounts to the same thing). The percentage of fat is subtracted from 3·0, multiplied by 100, and divided by 3, which gives the deficiency in fat.

If both the fat and solids-not-fat figures are low, the amount of added water should be first calculated, and a further calculation made to see if the addition of this amount of water would account for the lowness of the fat figure. If it does not, a further calculation must be made to determine the deficiency in fat.

Total Proteins.—These may be estimated by the Aldehyde Figure or by calculation from the total nitrogen. Kjeldahl's process for total nitrogen depends on the conversion of the nitrogenous matter into ammonium sulphate, which is decomposed by sodium hydrate, the liberated ammonia being distilled into standard acid, and the excess of acid titrated.

About 5 grammes of the milk are weighed into a round-bottomed, long-necked flask of about 300 c.c. capacity. The milk may be evaporated to dryness over a water-bath, the last traces of water being got rid of by drying in a water-oven and by gently blowing warm air into the flask. This drying process is tedious and is now usually omitted, although this may result in prolongation of the frothing period of the digestion. To the 5 grammes of milk are added 20 c.c. of concentrated sulphuric acid, and 5 to 10 grammes of potassium sulphate (in Gunning's modification), and the whole is heated for some time over a Bunsen flame. At first frothing takes place and then white fumes escape.

Up to this stage the neck of the flask may be held in a twisted towel in the hand in an inclined position while the flask is heated. This allows ready alteration in the degree of heat, and a careful worker is not inconvenienced by fumes. But when the acid fumes escape, or earlier, if the frothing is slight, the flask is placed in a fume-cupboard, in an inclined position, on a piece of wire gauze. Heating is then continued, cautiously at first, then quicker till the liquid boils. A bubble in the neck assists in preventing undue loss of acid.

The slanting position encourages condensation of the sulphuric acid vapours in the neck. When the liquid has become clear and colourless, or nearly so, the flask is allowed to cool; 200 c.c. of water are added, and the whole poured into the funnel of the distilling apparatus. A further quantity of about 200 c.c. of water is used to rinse out the flask; this also is poured into the funnel, and followed by 75 c.c. of 50 per cent. sodium hydrate solution. The stop-cock of the funnel is closed and heat applied; the ammoniacal steam is freed from splashings by its passage through the Soxhlet tube. With this apparatus the most troublesome substances can be dealt with.

The distillation apparatus is constructed as follows: A copper flask, capable of holding 1 litre, 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 or glass tube, $\frac{3}{8}$ inch in diameter, which is connected with a condenser, the end of which dips below the surface of 50 c.c. of decinormal acid in a 400 c.c. flask. Some workers dispense with a condenser, and either use a long length of block-tin tube or else a glass one. The whole of the distillation apparatus should be fitted up before the addition of the caustic soda to the liquid in the distillation flask.

The ammoniacal steam condenses in the tin tube, and is received in the acid. After about 250 c.c. 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 neutralised, methyl-orange, methyl-red, or cochineal being used as indicator. The last two can be used with artificial light.

Each cubic centimetre of $\frac{N}{10}$ sulphuric acid neutralised by the ammoniacal distillate corresponds to 0·0014 gramme of nitrogen.

A blank experiment should be performed, using the same quantities of materials, but leaving out

the milk, and the number of cubic centimetres of standard acid neutralised subtracted from that obtained in the determination.

The total proteins are estimated by multiplying the amount of nitrogen found by the factor 6·38 (Richmond's factor).*

As Self points out, if during the boiling with sulphuric acid and potassium sulphate too much free acid is used up, a loss in ammonia takes place; this becomes most serious when the liquid approaches the composition of potassium hydrogen sulphate.

Seven grammes of anhydrous sodium sulphate may, if convenient, replace the potassium sulphate (Latshaw). Many workers steam-distil the ammonia over. This is quite effective.

To accelerate the action of the sulphuric acid in the digestion flask, mercury is sometimes used, with addition of sodium sulphide when the digestion is completed. Nolte says this gives low results in some cases, and recommends use of copper foil in place of mercury. The Kjeldahl process does not estimate nitrogen present as nitrate, but can be modified to include it by the use of salicylic acid in the sulphuric acid in the digestion and the subsequent addition of sodium thiosulphate.

The 'Aldehyde Figure.'—Steinegger, who devised this method, titrated 100 c.c. of milk with the Soxhlet-Henkel $\frac{N}{4}$ normal soda solution till a pink colour with phenolphthalein was produced. At least 6 per cent. of 40 per cent. formaldehyde solution was added, and the acidity produced by the condensation of the amino groups of the proteins titrated. The amount of alkali consumed in the second titration, less the blank required by the formaldehyde added, gave the aldehyde figure.

Formaldehyde is nearly always acid; if neutralised with caustic soda and then diluted with neutral

* The proportion of nitrogen in different substances and in different proteins varies, necessitating the use of different factors. These are given in appropriate places in this book. Otherwise, the conventional factor of 6·25 may be used for conversion of nitrogen into protein (International Conference, Paris, 1910).

water, the solution becomes markedly alkaline. If strontia be used instead of soda, the reaction remains unaltered on dilution. For this reason and also because it gives a rather sharper end-point, Richmond and Miller (*Analyst*, 1906, p. 224) used strontia as the alkali and found it always to give a higher aldehyde figure, on an average 1·1 times higher, than when soda is used. The method as modified by Richmond (*Analyst*, 1911, p. 9) is as follows: To 10 c.c. of the milk are added 1 c.c. of a 0·5 per cent. phenolphthalein solution, and the milk is neutralised with $\frac{N}{11}$ (approximately*) strontium hydroxide solution; 2 c.c. of a 40 per cent. formaldehyde solution are then added, and the titration is continued until the same degree of pink coloration is obtained. After deducting the acidity of the formaldehyde solution, the amount used for the second titration represents the aldehyde figure, which is usually expressed as degrees or cubic centimetres of normal alkali required per litre.

The aldehyde figure, depending as it does on the content of amino groups, naturally varies with different proteins. But in cow's milk, where the ratio of casein to albumin is usually about 7 : 1, a factor for converting it into proteins is quite admissible. For strontia, Richmond calculated this to be 0·170.

The nature of the test renders it advisable that it should be done in duplicate or triplicate. The results, when carefully obtained, usually come within 0·2 per cent. of the figure obtained by multiplying the total nitrogen by 6·38.

Some workers still use soda, in which case a different factor must be used. Steinegger found that, on the average, 1 c.c. of decinormal soda corresponded to 0·0303 gramme of the nitrogen of milk; while Richmond and Miller (*Analyst*, 1906, p. 226), taking the mean proportion of casein to albumin to be 7 : 1,

* A saturated solution of strontium hydroxide varies with the temperature. In cold weather $\frac{N}{10}$ strength may be unattainable and a solution as weak as $\frac{N}{14}$ may have to be used. The solution therefore requires standardisation every time it is used.

found 0·0298 gramme. Taking the mean of these and using the 6·38 factor, a figure of 0·191 is obtained, with which the aldehyde figure as obtained by soda can be multiplied to obtain the amount of proteins. Among those using sodium hydroxide solution are de Graaff and Schaap, who found that the reaction of formaldehyde solutions does not change with dilution when this alkali is used unless the dilution is excessive. They, using Soxhlet-Henkel solution (*i.e.*, $\frac{N}{4}$ soda), deduced the factor 0·0777 for converting the aldehyde figure into nitrogen, or 0·495 for converting it into protein. Dividing these figures by 2·5, to bring them to the same denomination as the others, their factor for conversion of aldehyde figure into milk-proteins becomes 0·198.

Abnormal samples in which the process gives erroneous results are rare, but high results are obtained with sour milk, the rise above the truth depending on the extent to which hydrolysis of the proteins has occurred. However, Richmond (*Analyst*, 1908, p. 115) found that so long as the milk has not curdled, the change in the aldehyde figure is within the limits of experimental error.

In human milk the ratio of the proteins is different, and de Graaff and Schaap, using Soxhlet-Henkel soda denomination, found the nitrogen factor to be 0·0693, and the protein factor 0·443. Converting the protein factor to the English basis, it becomes 0·177.

The name 'aldehyde value' is not a scientific expression of the test, and Cecil Jones has suggested 'amino-acid number' as more intelligible.

Estimation of Lactose.—Pavy's solution is seldom used for this determination nowadays. Either the lactose is determined polarimetrically, or by one or other of the modifications of Fehling's test, volumetric or gravimetric. Before Fehling's solution can be used, the proteins and fat must be removed. When a gravimetric Fehling process is to follow, this may be effected by the process given by Blyth: 25 grammes of the sample are diluted with water, made almost neutral with sodium hydrate, and 10 c.c. of copper sulphate solution (that used for

preparing Fehling's solution—*i.e.*, 34·64 grammes per 500 c.c.) are added. The liquid is made up to 250 c.c. and filtered through a dry filter. This cannot be used when a volumetric Fehling follows, in which case the procedure given by Leach (also available for use when gravimetric estimation is proposed) may be followed: 25 grammes of milk in a 250 c.c. flask are treated with 0·5 c.c. of a 30 per cent. solution of acetic acid and the mixture well shaken. After standing for a few minutes, about 100 c.c. of boiling water are added. After well shaking the contents, 25 c.c. of alumina cream* are added, the flask shaken once more and then set aside for ten minutes. The supernatant liquid is poured over a wet folded filter, followed by the whole contents of the flask, and filtrate and washings are brought up to 250 c.c. The liquid should be perfectly clear.

A volumetric process can be carried out on the clarified solution by one of the methods described in the chapter on 'Sugar.'

There are a variety of gravimetric processes available for use, the one described below being that of O'Sullivan, further details being given in the chapter on 'Sugar.' Thirty c.c. of the mixed Fehling's solution is a suitable amount to use with 0·1 gramme of lactose. This is diluted with twice its bulk of water, and 25 c.c. of the clarified solution prepared in one of the above ways is a convenient quantity to use. The copper oxide (CuO) found is multiplied by 0·6024 (E. W. T. Jones's factor), which gives its equivalent of anhydrous lactose. Richmond dilutes the Fehling's solution with half the above amount (*i.e.*, an equal bulk of water), uses an anhydrous lactose factor of 0·6025, and deducts 2 milligrammes from the weight of the precipitate, when filter-paper has been used, as a correction for the amount of copper oxide absorbed by the filter from Fehling's solution.

* Alumina cream is prepared by adding a slight excess of ammonia to a cold, saturated, aqueous solution of alum. More of a cold saturated solution of alum is added till a faint acid reaction is reached.

Polarimetric Method of Determination of Lactose.—For further information on polarimetric work, reference may be made to the monograph on 'Sugar.'

The specific rotatory power of lactose at 20° C. is 52·5° when observed by the sodium flame. The rotatory power is unaffected by the degree of concentration within the limits met with in ordinary analytical work. It is but slightly affected by temperature, being decreased by about 0·042° for each successive rise of one degree of temperature.

When milk-sugar is freshly dissolved in water, it exhibits the phenomenon known as 'birotation,' or (more correctly) 'multirotation,' whereby it shows a higher rotation than that given above. By standing, or immediately on boiling and cooling, the rotatory power falls to normal. After dissolving solid milk-sugar, the solution should therefore be taken to the boiling-point before making up to a definite volume. This precaution is unnecessary when operating upon milk. In fact, the work of Richmond and Boseley (*Analyst*, 1893, p. 141) has shown the heating of milk to 100° C. to diminish the specific rotatory power of lactose. The polarimetric determination is consequently inapplicable to milk so heated.

To determine the amount of milk-sugar by means of the polarimeter, the proteins and fat must be removed. This is best done by means of mercuric nitrate, prepared as follows: Mercury is dissolved in double its weight of nitric acid of specific gravity 1·42, and an equal volume of water is added (Wiley's prescription, *Analyst*, 1887, p. 196).

According to Richmond (*Analyst*, 1910, p. 516) the use of phosphotungstic acid and sulphuric acid with the acid mercuric nitrate allows a higher figure to be obtained. Once dilute acid has been added to a lactose solution, it must not be warmed, nor left for any time before observation in the polarimeter, in case any lactose be converted into galactose, which has a higher specific rotatory power.

Richmond and Boseley (*Analyst*, 1897, p. 98) have considerably lessened the amount of calculation required in this process by the following device: To

every 100 c.c. of milk they add: (*a*) 3 c.c. of acid mercuric nitrate to compensate for the volume of proteins; (*b*) (fat + 1·11) c.c. to compensate for the volume of fat; (*c*) one-tenth of the degrees of specific gravity; (*d*) a sufficient volume to reduce scale readings to percentages of milk-sugar. (*d*) may be calculated by the formula $\left(\frac{55{\cdot}3\ \mathrm{K} \times l}{100} - 100\right) \times \mathrm{S}$, where K = factor necessary to convert angular degrees into scale readings, l = length of tube used, and S = specific gravity of sample (no appreciable error is introduced if this be taken as 1·032).

Using 50 c.c. of milk, the above process resolves itself as follows: 50 c.c. of milk are run into a dry flask, and a volume of water equal in cubic centimetres to the sum of (1) the degrees of gravity divided by 20, (2) the percentage of fat divided by 1·8, and (3) a quantity to convert scale readings into percentages of anhydrous sugar. If the scale is in angular degrees and a 200 millimetre tube is used, (3) is 5·43 c.c. (or 5 c.c. with a 198·4 millimetre tube). To the above mixture 1·5 c.c. of Wiley's acid mercuric nitrate solution (described above) is added, and the contents of the flask well mixed by violent shaking. The solution is poured on a dry filter and a polarimeter tube filled with the filtrate, which should be perfectly clear. The mean of several readings is then corrected for any deviation there may be for a tube filled with distilled water. If the latter is a plus reading, it is subtracted from, and if minus added to, the reading of the sample. The reading of the scale for the sample, thus corrected, gives the percentage by weight of anhydrous milk-sugar.

Example: A milk contains 3·7 per cent. of fat and has a specific gravity of 1·0325 (*i.e.*, degrees of gravity are 32·5). Then 2·05 compensates for fat, 1·62 compensates for gravity, and with a 200 millimetre tube and a polarimeter graduated in angular degrees an addition of 5·43 reduces the scale reading as required. The total water added is thus 9·10 c.c. and the 1·5 c.c. of acid mercuric nitrate solution compensates for proteins.

Preservatives.

Milk will keep sweet without preservatives, even in hot weather, for a period long enough to include a long railway journey, delivery to customers, and a period at the consumer's house that will allow of its consumption. This is particularly true of milk which is protected from avoidable contamination, and which after being drawn from the cow, has been sieved and cooled.

The use of preservatives protects dirty milkmen and farmers by allowing soiled milk that would otherwise quickly become obviously unsound to retain its fresh appearance for a longer period.

With the possible exception of hydrogen peroxide, the chemical preservatives used in milk have probably all a detrimental action on the system. This objection carries special force in the case of infants, who are generally more susceptible than adults to small doses of toxic substances. There is considerable evidence to show that preservatives retard the digestion of food, and conduce to indigestion. In certain diseases such as typhoid and diphtheria, large quantities of milk are commonly taken with a correspondingly greater quantity of any preservative. Further, there are pathological conditions, such as nephritis, where the ingestion of boric acid seriously affects the condition of the patient.

In 1906 a circular was issued by the Local Government Board, who therein mention that ' the presence in milk of formalin to an amount which is ascertained by examination within three days of collecting the sample to exceed 1 part in 40,000 (1 part of 100,000 of formic aldehyde), raises a strong presumption that the article has been rendered injurious to health, and that the purchaser has been prejudiced, in the above sense; and also that similar presumption is raised where boron preservatives are present in milk to an amount exceeding 57 parts of boric acid per 100,000, or 40 grains of boric acid per gallon.'

The Public Health (Milk and Cream) Regulations. 1912, issued by the Local Government Board, *inter*

alia, provide that 'no person shall add, or order, or permit any other person to add, any preservative substance to milk intended for sale for human consumption, and that no person shall sell, or expose, or offer for sale, or have in his possession for the purpose of sale, any milk to which any preservative substance has been added.'

Borates.—Boric acid and borax are seldom used separately for food preservatives; generally the two are mixed with common salt and the relative proportions vary greatly. To detect boric acid, the ash of the milk is treated with a few c.c. of water and a little dilute hydrochloric acid, so that it is distinctly, but not strongly, acid; a piece of turmeric paper is placed in the liquid, and the dish is slightly warmed for a few minutes. The turmeric paper is removed and dried at a low temperature. If 0·01 per cent. of boric acid be present, it will produce on the paper a reddish colour when dry. On moistening with a drop of an alkali solution (semi-normal is quite a suitable strength), the red turns a greenish-black.

To prevent loss of boric acid during evaporation and ignition, the milk may first be rendered alkaline with lime-water. Alternatively, milk may be tested direct. To 5 or 6 c.c. 1 drop of strong hydrochloric acid is added and stirred in. A piece of turmeric paper is immersed in the curdled milk, which is warmed till steam rises. The test-paper is removed, any adherent curd brushed off, and the paper dried at a low temperature. Complaints that turmeric paper sometimes gives a red colour when no boric acid is present may arise from the use of paper contaminated with it. The red colour is only developed when the paper is quite free from moisture, and ordinary humidity would leave sufficient moisture on contaminated test-paper to prevent the colour appearing before use. A more common cause of redness in the dried paper arises from the use of too great a proportion of hydrochloric acid. This need never lead to error, as not only does the acid tint differ in shade from the true boric colour, but it is not turned greenish-black by alkali, and such paper

will, when dry, often crumble or break if creased between the fingers.

Turmeric paper is prepared by soaking filter-paper in an alcoholic extract of turmeric and drying. The addition of oxalic or tartaric acid increases the sensitiveness, and a process based on the use of such paper for the approximate determination of boric acid in milk has been devised by Cribb and Arnaud (*Analyst*, 1906, p. 147). A turmeric paper is made by digesting 2 parts by weight of turmeric and 2 parts of tartaric acid with 100 volumes of about 80 per cent. hot alcohol until all the tartaric acid has dissolved. Fairly thick blotting-paper is saturated with the filtered tincture and hung up to dry in the dark. Paper made in this way turns with strong solutions of boric acid a bright rose-pink colour, and the same colour is still just apparent when the dilution is as great as 0·0025 per cent. It is desirable that the turmeric paper should be fresh.

Boric acid in milk may be estimated by Thomson's method as follows: 1 to 2 grammes of sodium hydrate are added to 100 c.c.of milk, and the whole evaporated to dryness in a platinum dish. The residue is thoroughly charred, heated with 20 c.c. of water, and hydrochloric acid added drop by drop until all but the carbon is dissolved. The whole is transferred to a 100 c.c. flask, the bulk not being allowed to get above 50 to 60 c.c., and 0·5 gramme dry calcium chloride* added. To this mixture a few drops of phenolphthalein solution are added, then a 10 per cent. solution of caustic soda, till a permanent slight pink colour is perceptible,† and finally 25 c.c. of lime-water. In this way all the phosphoric acid is precipitated as calcium phosphate. The mixture is made up to 100 c.c., thoroughly mixed, and filtered through a dry filter. To 50 c.c. of the filtrate (equal to 50 grammes of the milk), normal sulphuric acid is added till the pink colour is gone, then methyl

* Two c.c. of 50 per cent. calcium chloride is preferable.

† The tendency of carbon particles to adsorb phenolphthalein and thus remove it from solution may result in a large and needless excess of alkali being added, unless the worker is awake to the possibility.

orange is added, and the addition of the acid continued until the yellow is just changed to pink. Fifth-normal caustic soda is now added till the liquid assumes the yellow tinge, excess of soda being avoided. At this stage all acids likely to be present exist as salts neutral to phenolphthalein, except boric acid, which, being neutral to methyl orange, exists in the free condition, and a little carbonic acid, which is expelled by boiling for a few minutes. The solution is cooled, a little phenolphthalein added, and as much neutral glycerin* as will give at least 30 per cent. of that substance in the titrated solution, and titrated with fifth-normal caustic soda till a distinct permanent pink colour is produced; each cubic centimetre of fifth-normal soda is equal to 0·0124 gramme of boric acid. A series of experiments with this process showed that no boric acid was precipitated along with the phosphate of calcium so long as the solution operated upon did not contain more than 0·2 per cent. of boric acid, but when stronger solutions were tested, irregular results were obtained. The charring of the milk is apt to drive off boric acid, but by carefully carrying the incineration only so far as is necessary to secure a residue which will yield a colourless solution, no appreciable loss occurs.

Formaldehyde (HCOH).—This is usually met with in the form of a 40 per cent. solution, 'formalin.' Two or three drops keep a pint of milk fresh for three or four days.

Formaldehyde is incidentally detected when the Gerber or Leffmann-Beam methods for fat are used, if present in amounts over 0·0002 per cent., and also by the following methods:

Hehner's Method.—About 3 c.c. of the milk are run into a test-tube and diluted with an equal volume of water. Then 90 per cent. commercial sulphuric acid is carefully run down the side of the test-tube (which should be held in a slanting position), so that

* Mannitol in a proportion of at least 2 per cent. of the bulk titrated may replace glycerin, but after the titration a further addition of mannitol should be made to make sure that sufficient is present.

it forms a distinct layer at the bottom. In the absence of formaldehyde a slight greenish tinge is given at the junction of the liquids, and after some hours a brownish-red colour is developed a little below the junction. If formaldehyde be present a violet ring is formed at the junction of the two liquids. Pure sulphuric acid will not give the reaction, but it will after the addition of a little ferric chloride. This test will detect 1 part of formaldehyde in 200,000, but the blue coloration is not obtained with milks containing over 0·5 per cent. This is stated by Rosenheim to be due to the strong reducing power of the formaldehyde being exerted towards the oxidising agent, and the reaction fails in proportion to the amount of oxidising agent present. In milk, formaldehyde is gradually decomposed, and it is necessary to test for it at the earliest opportunity. After a few days it may fail to respond to tests.

Jorissen's Test.—To 10 c.c. of milk in a test-tube are added several drops of a 10 per cent. aqueous solution of phloro-glucinol, the mixture shaken, and a few drops of a solution of sodium or potassium hydrate are added. Normal milk gives no reaction, but a milk containing as little as 1 part of formalin in 20,000 gives a fleshy-pink coloration.

Estimation of Formaldehyde in Milk.—A really satisfactory method of estimating formaldehyde in milk has not been produced. On account of the rapid disappearance of formaldehyde, an amount less than that added is invariably obtained. A process, by Shrewsbury and Knapp, is given in the *Analyst*, 1909, p. 12. A reagent is made by mixing 0·1 c.c. of pure nitric acid with 100 c.c. of concentrated hydrochloric acid. To 5 c.c. of milk in a test-tube (about 18 centimetres by 2 centimetres) 10 c.c. of the *freshly-made* reagent are added, the mixture shaken vigorously, and kept for ten minutes in a water-bath at a constant temperature of 50° C. The tube and its contents are then cooled rapidly to about 15° C. A violet colour shows the presence of formaldehyde, and its intensity indicates the amount, which may be estimated by means of standards put

on at the same time. If the colour obtained is deeper than that shown by 6 parts of formaldehyde per million of milk, a dilution of the sample with pure milk is recommended. The most delicate quantitative reaction is obtained with milks containing 0·2 to 6 parts per million of formaldehyde.

The tubes must not be allowed to touch, or even come near, the bottom of the water-bath, for then the temperature of the bottom of the tubes will be raised above 50° C., and colours simulating those of formaldehyde will be produced by the action of hydrochloric acid on the lactose. A pure milk must always be treated at the same time and in precisely the same way; only if this gives an absolute blank can the lower amounts of formaldehyde be shown.

The statement made above, that the Hehner test fails in the presence of excessive amount of an oxidising agent, requires qualification. Some oxidising agents can be used in much greater proportion (to formaldehyde) than others without lessening the delicacy of the test. One preservative offered to the milk trade under the name of 'mystin' contained, besides 0·30 per cent. of formaldehyde, 9·85 per cent. of sodium nitrite. Milk to which this had been added did not give the Hehner test for formaldehyde. G. W. Monier-Williams, reporting to the Local Government Board (Food Reports, No. 17), considered it probable that some reaction occurs between nitrous acid and the tryptophane which is present among the products of hydrolysis of milk casein. To remove the influence of the nitrous acid, he treats 5 c.c. of milk with 0·05 gramme of urea and 1 c.c. of normal sulphuric acid, heats in a boiling water-bath for two minutes, and cools. If the milk contained 'mystin,' a positive Hehner test may be obtained, if the formalin has not disappeared, and formalin may be estimated by the Shrewsbury-Knapp process in milk similarly treated.

A suspicion that nitrite is present may be raised during the estimation of fat by the Leffmann-Beam or Gerber methods. Instead of the usual gradual development of a purplish-brown colour on mixing with the sulphuric acid, a light yellow is followed

by a golden-yellow colour of noticeable persistence, which later turns to an amber-brown. The addition of a solution of meta-phenylene-diamine hydrochloride to the milk after acidulation with sulphuric acid (Griess's test), if nitrite be present, produces a buff to amber colour which strengthens on standing. The Griess-Ilosvay reagent gives a pink colour (see chapter on 'Flour') with milk containing nitrite. By comparison of the colour with that produced under identical conditions in milk containing standard nitrite, an approximate estimation of the amount of nitrite present can be obtained.

We have shown that sodium nitrite may be detected by the benzidin test for hydrogen peroxide (*q.v.*). In the presence of sodium nitrite, the alcoholic benzidin solution strikes a transient brilliant blue colour with the diluted milk, and, after acidulation with acetic acid, a deep orange colour develops in a few minutes which fades to a yellow in the course of twenty-four hours.

H. D. Gibbs found the Hehner test for formaldehyde unsatisfactory in the presence of hydrogen peroxide. After removal of hydrogen peroxide by means of reducing agents (sodium hydrogen sulphite and sulphur dioxide), positive tests were obtained. This mixture is a feature of a commercial preservative.

Fluorides.—The fluorides or silico-fluorides of sodium or potassium have been used for the preservation of milk and cream. They are to be detected by the methods described under 'Butter,' but the titanium test is much less significant in positive reaction with milk than it is with butter. This is especially the case with condensed milk, which gives a positive test in most cases where fluorides are shown to be absent by the etching test. For analyses of preservatives of this type see Local Government Board Food Report No. 17, and Report of their Medical Officer for 1912-13, p. 277. Richmond (*Analyst*, 1907, p. 146) has shown that more than 0·1 per cent. of sodium fluoride is necessary before the slightest preservative action is effected. P. A. E. Richards (*Analyst*, 1914, p. 248) proved the liberation of fluorine from fluorides by weak acids.

As the evidence shows that fluorides replace phosphate in bone, the use of them in food is to be most strongly reprehended.

Salicylic Acid.—The use of salicylates as milk preservatives has ceased in this country, and is not likely to recur unless some means of disguising the taste is found.

Salicylic acid may be detected by Hinks's test for benzoates and will also be found by precipitating the casein by the addition of acetic acid, filtering, and adding ferric chloride to the filtrate.

Sodium Bicarbonate.—Where this has been added in fair quantity the ash of the milk will effervesce on the addition of dilute acid, and can be estimated by titrating the ash with decinormal acid. The ash of 5 c.c. of normal milk does not require more than 0·3 c.c. $\frac{N}{10}$ HCl, and any excess of alkalinity over this may be taken as sodium carbonate.

Sodium carbonate may also be detected by mixing 10 c.c. of the milk with an equal quantity of rectified spirit in a test-tube, and adding 2 or 3 drops of a solution of rosolic acid (1 gramme in 25 c.c. of alcohol, diluted to a litre with distilled water). A rose-pink indicates the presence of sodium carbonate.

Benzoates.—The sodium salt has been and probably still is sold as a milk preservative under various fancy names. It may be detected by Hinks's method (*Analyst*, 1913, p. 555) if 0·01 per cent. be present: 25 c.c. of the milk, or from 10 to 20 grammes of the cream, are heated with an equal volume of concentrated hydrochloric acid until the curd has dissolved completely. The mixture is cooled, and shaken with 25 c.c. of a mixture consisting of 2 volumes of light petroleum and 1 volume of ether. The ethereal solution is separated, and on the addition of 1 drop of ammonia (0·880), precipitation of ammonium benzoate as a white haze results. (A similar haze is given with salicylic acid.) Five c.c. of water are added and the mixture shaken. The aqueous layer is separated, heated on a water-bath for a few minutes to expel the excess of ammonia, and then tested with ferric chloride solution. A buff-coloured precipitate shows the presence of a benzoate.

The process can be made quantitative by heating 25 c.c. of the milk with hydrochloric acid under a reflux apparatus, extracting the cooled solution three times with 20 c.c. of the mixture of light petroleum and ether, and shaking the separated ethereal portions with 10 c.c. of water and 1 drop of ammonia; this extraction is twice repeated. The mixed aqueous portions are then acidified with hydrochloric acid, extracted three times with the ethereal solvent, the extracts are evaporated at the ordinary temperature, and the residue is dried in a desiccator to constant weight. The benzoic acid is then volatilised at 100°, the loss in weight giving the amount of the acid.

Hydrogen Peroxide.—When added to milk, hydrogen peroxide is attacked by catalase, to the total destruction of whichever of the two is present in the smaller proportion and the correspondingly proportional destruction of the other. Should the catalase (see 'Milk Enzymes') present be capable of destroying more peroxide than is added, the latter disappears and tests for its presence are negative. But if the quantity of peroxide exceeds the splitting power of the catalase, it will persist for over a year (Hinks, *Analyst*, 1915, p. 482). The reactions given below depend on the presence of peroxidases in the milk, which enzymes are destroyed by this preservative. It is sometimes necessary to add fresh milk to the sample before a positive reaction can be obtained (Hinks, *loc. cit.*). For the same reason, fresh milk must be added to the sample if the latter has been heated.

Hydrogen peroxide leaves a peculiar taste in milk and is not likely to be used. The taste can be removed by the addition of yeast extract: a procedure of doubtful advisability.

Benzidin Acetate Test.—Ten c.c. of milk are diluted with an equal volume of water and 0·4 c.c. of a 4 per cent. solution of benzidin in alcohol is added, followed by 0·2 c.c. of acetic acid. The mixture is shaken. A blue colour, sometimes of a greyish tint, shows the presence of hydrogen peroxide. This may take a few minutes to develop if the amount of preservative is small. An orange colour of a slow-

developing type would suggest the presence of a nitrite (*q.v.*).

We find that if the benzidin tincture be not less than two or three weeks old, a peacock-green colour develops as the reagent comes in contact with the milk if the latter has not been heated. If the milk has been heated, only the brown colour of the benzidin solution is seen. The peacock-green colour disappears on mixing. The use of an old tincture not only answers the same purpose as a newly-made one, but also shows whether the enzymes necessary for the production of positive tests are present, or whether it is necessary to add fresh milk.

The tests described for heated milk may be adapted to the detection of hydrogen peroxide, by omitting the addition of it.

Pasteurisation.—Milk can be heated to a temperature sufficient to kill the less resistant pathogenic bacteria, without altering the flavour. The temperature varies from 70° to 85° C., the latter temperature being that suggested as desirable by Professor Bang, Sir John McFadyean, and the Board of Agriculture. The milk is kept at the high temperature for fifteen minutes, or at the lower temperature for thirty minutes, and then quickly cooled. This destroys the pyogenic cocci, the virus of foot-and-mouth disease, the cholera vibrio, the tubercle bacillus (sometimes), and typhoid bacillus. Pasteurisation, if properly done, destroys over 90 per cent. of the total number of organisms. As those which produce lactic acid are destroyed, Pasteurised milk may decompose without souring. The sporulating organisms which survive are in some cases capable of producing toxic substances. In unheated milk these organisms would be checked by the lactic acid bacilli. Pasteurised milk should therefore be consumed within eighteen or twenty-four hours—*i.e.*, before sporulating bateria have time to multiply to an objectionable extent. The heating may conceal a certain degree of putrefaction which had previously taken place.

Contrary to previous belief, caseinogen digestibility is now thought to be increased by heating, part of the

albumin may be precipitated, lactose is unaffected, while calcium and phosphorus are partly thrown out of solution. The effect on the fat content is uncertain.

Storch's (or Dupuoy's) Method for Detection of Heated Milk.—To 5 c.c. of milk in a test-tube are added a drop of hydrogen peroxide solution (about 0·2 per cent.) and 2 drops of a 2 per cent. solution of para-phenylene-diamine. The tube is shaken. If the milk becomes indigo-violet, the milk has either not been heated at all, or else not heated above 78° C. If the milk has been heated above 80° C., the colour remains white. Saul uses 'Ortol' for the purpose, which gives a deep red.

Arnold's Test.—A little milk is placed in a test-tube, and a 5 per cent. alcoholic tincture of guaiacum is dropped on the surface of the milk, so that the liquids mix slightly. If the milk has been heated to 80° C. no colour appears, but in the case of unheated milk a blue zone is formed at the junction of the two liquids. Fresh tincture of guaiacum will not give the reaction, it being necessary to allow it to suffer a degree of oxidation by exposure to light and air for eight or ten days. Fresh tincture of guaiacum will act if hydrogen peroxide be added as well.

In using these tests, comparative tests with heated and unheated milk at the same time as the sample is under examination should always be made to ascertain the suitability of the reagents.

Milk Enzymes.—Some of the ferments found in milk are derived from the mammary gland itself, others result from bacterial growth in the milk.

Harden and Lane-Claypon (*Journal of Hygiene*, 1912, p. 144) demonstrated the presence both of peroxidase (an enzyme acting on peroxides) and catalase (which breaks up hydrogen peroxide with production of oxygen) in milk obtained by catheter from both goats and cows. Peroxidase is derived from leucocytes (Gillet), while the catalase present in milk from the healthy gland is thought by Lane-Claypon to be almost certainly derived from the blood by a process of filtration.

Spindler found the catalase content to be greater

in sour than in fresh milk, and to increase with the age of the milk. Or, to put it in another way, the catalase increases with bacterial growth. In commercial milk, that due to bacteria is generally much greater than that from the gland. Sour milk products (youghourt and kephir) also contain more catalase than fresh milk.

Inflammatory conditions of the udder usually, but not always, increase the catalase content, which has been regarded as an indication of udder disease. While it has some degree of usefulness for this, the bacterial catalase may render the test fallacious.

An index of the degree of catalytic activity can be obtained by Koning's iodometric method as used by Revis (*Analyst*, 1910, p. 359): In each of two stoppered flasks of 250 c.c. capacity 5 c.c. of milk are placed, and to one 6 drops of hydrochloric acid (1 : 1) is added to destroy the enzyme; 5 c.c. of 1 per cent. hydrogen peroxide is added to each, and the flasks kept at 38° C. for two hours. Ten c.c. of strong hydrochloric acid are added, shaking well, and then 10 c.c. of 10 per cent. potassium iodide, and after fifteen minutes 100 c.c. of water. The liberated iodine is titrated with $\frac{N}{10}$ thiosulphate, with starch paste as indicator. Owing to the occlusion of iodine by the casein, the titration takes about thirty minutes. The difference between the two titrations, calculated as c.c. of decinormal thiosulphate per 100 c.c. of milk, gives the catalytic activity.

Lane-Claypon, reviewing the work on the subject ('Milk and its Hygienic Relations'), came to the following conclusions regarding protease, lactase, lipase, amylase, and salolase: Proteolytic enzymes and lactase (lactose-fermenting enzyme) are either absent from milk as it leaves the udder, or, if present, are without appreciable digestive ability. Lipase (fat-splitting enzyme) is thought to be absent from cow's milk, and though one has been demonstrated in human milk, its action is restricted to such glycerides as monobutyrin. She regards as filtrate from the blood, the trace of amylase (starch-converting enzyme) thought to be present in bacteria-

free milk. No enzyme acting on salol (salolase) is found in cow's milk.

Speaking generally, Lane-Claypon (*loc. cit.*, p. 226) considers there to be no reason to suppose that ferments when present in milk are of any value.

Schardinger's reagent (5 c.c. of a saturated alcoholic solution of methylene blue, 5 c.c. of formaldehyde, and 190 c.c. of water) is stated (*Analyst*, 1906, p. 157) to be invariably decolourised by a milk that has never contained hydrogen peroxide; but a milk that has been so treated loses its power of decolourising the reagent, and only regains it again when bacterial decomposition has commenced. The decolourisation takes place in a few minutes at 45° C., and, as it is not given if milk has been first boiled, is presumed to depend on an enzyme referred to as 'indirect reductase.' It can be obtained with milk free from bacteria, but not with milk in the early stages of lactation. The first milk drawn from the udder does not decolourise Schardinger's reagent, whereas, as a rule, the milk obtained at the end of the milking does (Römer). Boiled milk, to which a small quantity of alkali or ferrous sulphate solution has been added, gives a positive reaction. Schardinger's reagent is not reduced by goat's milk, but catheter milk from the cow frequently reduces it (Harden and Lane-Claypon).

Many of the bacteria that find their way into milk produce reducing enzymes (reductases), and the milk reduces a simple methylene blue solution (direct reductases). The test has been advocated as an index of bacterial population, ignoring the fact that many bacteria do not produce reductases. This reduction of simple methylene blue is not given by catheter milk. In conjunction with other tests, it has been used for determining the fitness of milk for condensing purposes and margarine-making.

It is not thought likely that peroxidase is ever bacterially produced in milk, but a reducing enzyme (hydrogenase) that produces sulphuretted hydrogen has been detected.

Dirt in Milk.—Although milk is usually strained after milking to remove the grosser particles of dirt,

it is likely to become subsequently contaminated with visible particulate matter, and a certain amount of dirt would pass the strainer. This dirt can be separated by centrifuging (or allowing to stand), siphoning off the bulk of the milk, and washing the residue a few times by adding water and allowing to stand for a few hours. When the wash-water is clear, the deposit is weighed on a tared filter. Thresh gives 3 to 5 milligrammes as the amount given by a litre of really clean milk. In Dresden, a milk must not contain more than 8 milligrammes per litre. Houston, in 1905, suggested two standards for dirt: (1) the amount of filth that settles on standing (to be less than 100 parts by volume per million); (2) the apparent filth in (1) is diluted with water and centrifugalised (volume of apparent filth to be less than 50 parts per million). In the Farmers' Milk Competition (Royal Agricultural Society) disqualification followed if more than 3 parts of dirt or 35 of slime in 100,000 parts (volume) of milk were found. W. F. Lowe added dung to milk and found that he only extracted one-eighth of it afterwards in the dry form. The remainder, being soluble, had dissolved.

The nature of the dirt can be ascertained by mounting in dilute glycerin and examining microscopically. It may thus be found to contain particles of fæcal matter, iron rust, epithelial cells, blood-cells, pus, cow hairs, particles of mineral matter, and of hay, straw, and so on. For further information on the sediment of milk and examination thereof, see Moor and Partridge, 'Aids to Bacteriology.'

We find the most ready method for the identification of any brown particles as dung in rubbing up a portion on a microscope slide, drying, fixing and staining by Gram's method. We examine the preparation for streptococci, which retain Gram's stain. A brown particle containing large numbers of streptococci is almost certainly dung. Salivary streptococci would not occur in particles, and those in pus would be in a creamy deposit. While this method would hold for the excreta of cow, horse, and sheep, it might fail with pig dung. When the dung is stale, it is sometimes held together by the

mycelia of moulds. W. F. Lowe, describing the residue of cow dung obtained from milk as usually undigested vegetable fibre and tissue stained yellowish with bile, modifies Pettenkofer's test to detect the bile. He moistens the sediment with sugar solution, dries the mixture, and adds a drop of sulphuric acid. A red colour develops round the particles stained with bile.

Synthetic 'Milk.'—An article, said to be of vegetable (including soja bean) origin, has been introduced as a substitute for milk. It is said to contain 3·65 fat, 4·85 sugar, 3·85 albuminous matter (casein), and 0·67 mineral matter, besides other ingredients.

Colouring Matters.—Milk is very extensively coloured with dyes in this country, the most common one found being annatto, but coal-tar dyes of the azo type are met with, and saffron, turmeric, and carrot-juice are likely to be used. Although a dye gives milk the fictitious appearance of 'richness,' and may in certain cases be used with fraudulent intent to cover the addition of water or skimming, there is little doubt that most dairymen use dyes simply because discontinuance of their use would cause complaints about the 'poorness' of the milk. The Departmental Committee on Preservatives and Colouring Matters thought the practice appeared to be highly undesirable, and that 'the purchaser is entitled to be aware of the natural colour, and to draw his own conclusions therefrom as to quality.'

Annatto may be detected by adding to the milk a little bicarbonate of sodium, immersing therein a strip of white filter-paper, and allowing to stand overnight. A brownish stain will be visible on the filter-paper next morning. (See also *Analyst*, 1898, pp. 174, 229, 230.) A dilute mineral acid added to milk containing a coal-tar dye of the azo group produces a pink colour. There appears to be some evidence that, while the annatto is apparently harmless, the ingestion of a coal-tar dye may not be free from injurious effects.

HOMOGENISED MILK.

To prevent the fat rising freely, milk is sometimes passed through a machine which very greatly diminishes the size of the fat globules. Under a pressure of from 200 to 400 atmospheres the milk is forced through very small openings, so that the fat globules do not generally exceed 0·001 millimetre in diameter. Droop Richmond has shown (*Analyst*, 1906, p. 218) that, while the Gottlieb, Kieselguhr, Werner-Schmid, and Gerber methods give good results in the estimation of fat in homogenised milk, the results obtained by the Adams method are consistently low. He attributes this to the film of homogenised milk on the Adams coil being of sufficient thickness for some of the fat globules to be completely surrounded with a layer of solids insoluble in ether.

DRIED MILK.

Milk in the powdered form is prepared in several ways. In one process the milk is evaporated by passage over revolving steel cylinders heated to 230° F., while in another process the milk is condensed in vacuum pans, and finally dried in thin layers in a vacuum chamber. To reconstitute the milk the powder is made into a thin paste with water, and hot water is added to bring it to the right volume. To facilitate the solubility of the dried milk, such additions as sodium carbonate, calcium saccharate, glucose, or sodium phosphate are added.

Eric Pritchard (*Medical Press*, February 25, 1914) says that the tallowy smell of Bévenot-de-Neveu milk is due to the oxidation of the fat, which in no way affects the nutritive value of the milk. In all other respects Pritchard regards Bévenot-de-Neveu milk as superior to other varieties of desiccated milk.

David Sommerville (*Public Health*, 1905, p. 40) in a series of artificial digestions found the fat and proteins to be in a more soluble form than in ordinary milk. When curdled with rennet or by dilute acid,

the curd is formed as fine flakes, and not in a single large clot, as in ordinary milk.

Dried milk is largely used for infant-feeding. It is readily digested, is not liable to contamination by micro-organisms, whether dust-borne or by flies; it keeps perfectly during the warmest weather, and can be freshly prepared for each meal.

The analysis of milk powders requires slight modifications of the processes adopted for the analysis of milk. Moisture is determined on a small quantity—1 or 2 grammes. Droop Richmond selects 6·87 as the correct factor for proteins (*Analyst*, 1906, p. 220). Pritchard says the acidity of dried milk is only plus 4·5* (Eyre's scale).

The fat is best determined by the Röse-Gottlieb method. To 0·5 to 0·7 gramme of the dry milk sufficient water is added to make up a weight of 5·15 grammes; 0·5 c.c. of ammonia is added and the dry milk dissolved by shaking, and, if necessary, slight warming; 5 c.c. of alcohol are added and the process continued as described on p. 28.

In both Western Australia (1913) and Natal (1914), dried milk is not permitted more than 5 per cent. moisture.

CREAM.

Cream used to be prepared simply by allowing milk to stand overnight and skimming off the cream next morning. It is now extensively prepared by centrifugal action, by which the milk is almost entirely deprived of its fat, and the cream contains a much higher percentage of fat (from 45 to 65 per cent.).

Devonshire, Cornish, or clotted cream is prepared by warming milk in pans for several hours. The cream rises to the top in a much more coherent layer and more rapidly than when the milk is merely

* 'Eyre's scale' is the denomination of reaction used in bacteriology. When plus, it represents acidity in terms of normal acid per litre. Phenolphthalein being used as the indicator, the figure is consequently the same as if returned as 'degrees of acidity.'

allowed to stand at room temperature. Such cream will contain from 50 to 60 per cent. of fat. Tinned cream is usually a less valuable article, its fat content being, say, from 23 to 35 per cent.

Artificial Thickening Agents.—To deceive the purchaser as to its fat content, recourse is sometimes had to such thickening agents as gelatin, starch paste, saccharate of lime (a saccharine solution of lime known as ' viscogen '), and condensed milk.

If gelatin be in any considerable quantity, the cream assumes a buttery consistency, and it will no longer pull out into strings, as will a genuine rich separated cream. Gelatin may be detected by carefully drying a portion, removing the fat with ether, and taking up the residue with the least possible quantity of boiling water. On allowing to cool, if gelatin is present the liquid will set solid.

Another method, for which we are indebted to Mr. A. W. Stokes, depends on the precipitation of gelatin by tannin. Mix a weighed quantity of the suspected sample with warm water, and add acetic acid to precipitate fat and proteins, taking care to avoid excess, filter, and to the clear liquid add a few drops of strong solution of tannin. A sample of genuine cream should be treated in the same way for comparison. On addition of the tannin solution, a slight precipitate is produced in the case of genuine cream; but in a sample adulterated with gelatin a copious precipitate will be thrown down.

For the detection of small quantities of gelatin Stokes's method (*Analyst*, 1897, p. 320) should be used: Dissolve some mercury in twice its weight of strong nitric acid (specific gravity 1·42); dilute this with water to twenty-five times its bulk. To about 10 c.c. of this solution add a like quantity of cream and about 20 c.c. of cold water. Shake vigorously, allow to stand for five minutes, and filter. If much gelatin be present it will be impossible to get a clear filtrate. To the filtrate add an equal bulk of a saturated aqueous solution of picric acid, when a yellow precipitate will be immediately produced in the presence of gelatin. The whole operation is performed in the cold. If the cream is sour, turbidity

may occur in the absence of gelatin. A. Seidenberg (*Analyst*, 1914, p. 33) proposes an extension of the process.

Starch may be detected by the blue colour produced on the addition of a solution of iodine in potassium iodide.

In the amount in which it is used, calcium saccharate will only raise total solids 0·19 per cent. and the ash 0·04 per cent. The determinations therefore give no clue to its presence or absence. It is detected by estimating the percentage of lime in the ash (the average percentage of CaO being 22·4 per cent. of the ash). (See also *Analyst*, 1908, p. 401.) Viscogen will also cause the percentage of sugar polarised as milk-sugar to exceed 52·5 per cent. of the solids-not-fat. As cane-sugar is sometimes a constituent of the boron preservatives sold for the preservation of cream, its presence will not necessarily indicate the presence of calcium saccharate.

Anderson (*Analyst*, 1907, p. 87) recommends Cayaux's test for the detection of cane-sugar. Fifteen c.c. of milk, or 15 c.c. of cream, are mixed with 0·1 gramme of resorcinol and 1 c.c. of strong hydrochloric acid, and the mixture is raised to the boiling-point. In the presence of cane-sugar a fine red colour is produced. Pure milk is but slightly affected, and only turns a brownish colour on boiling.

Colouring Matters.—Cream is occasionally coloured with annatto and with coal-tar dyes, which may be detected by the methods given in the chapter on 'Milk.' Annatto is present in one of the calcium saccharate preparations.

Fat. — The fat is estimated by weighing out 2 grammes into a small dish, thoroughly mixing with about 12 c.c. of water, pouring into a Leffmann-Beam bottle, and treating in the same way as ordinary milk. The result obtained is multiplied by the factor 7·77. The fat in cream might also be estimated by the Werner-Schmid method, or by an extraction of the total solids with ether.

Preservatives.—Sodium carbonate is sometimes added to delay souring. The solution of lime in cane-sugar syrup, already referred to, acts in the same

way. Such articles cloak conditions that would in their absence prevent the cream being used.

Formaldehyde, sulphites (rarely), sodium meta-bisulphite (Monier-Williams), sodium fluoride, salt, and saltpetre have also been employed. A mixture of boric acid and borax is, however, by far the most frequent. The methods described under the Detection of Preservatives in Milk apply also to cream.

Hehner's test for formalin can be regarded as positive only when the purple ring appears within twenty minutes. An apparently typical ring is given by pure cream if allowed to stand longer than this.

A negative test for boric acid with turmeric paper is always to be regarded as inconclusive. In the first place, the fat may protect the test-paper from the action of the boric acid, or, even should the reaction occur and the red colour develop on drying the test-paper, the fat picked up may protect the paper from the action of alkali and thus raise the false presumption that, as no greenish-black colour has developed, borates cannot be present. Cream not giving a positive reaction on direct testing should always be evaporated to dryness after alkalisation with lime-water, ignited, and tested after acidulation in the usual way.

For the estimation of boric acid, 10 grammes of cream are mixed with 20 c.c. of water and brought to the boil. After the addition of phenolphthalein, decinormal soda is run in till a faint but distinct pink tint is attained. About 0·7 gramme of mannitol (or 18 c.c. of neutral glycerin) is added and the addition of the soda continued till pink again appears. The number of cubic centimetres of decinormal alkali added *subsequent to the addition of mannite* if multiplied by 0·0062 will give the amount of boron compounds in terms of boric acid in the 10 grammes taken.

The Public Health (Milk and Cream) Regulations, 1912, made under the Public Health (Regulations as to Food) Act, 1907, by the Local Government Board, prohibits all preservatives in cream containing less than 35 per cent. of milk fat. Cream containing over 35 per cent. may contain boric acid provided

its presence and amount is disclosed by label; an addition of peroxide of hydrogen may also be made provided that disclosure of the addition is made on the label.

The Public Health (Milk and Cream) Regulations, 1912, Amendment Order, 1917, prescribes that not more than 0·4 per cent. of boric acid may be added to cream, and it must be sold as 'preserved cream.' Also that both in the case of cream containing boric acid and that containing peroxide the declaratory labels must bear the words 'Not suitable for infants or invalids.'

CONDENSED MILK.

Many of the brands at present on sale in this country are the same milk under different labels. 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. In the case of even the best condensed milks, prepared from genuine milk with all its fat, the directions for dilution are very open to criticism.

1. The unsweetened milks are well prepared, and keep perfectly. They contain the due proportion of fat.

2. The sweetened class forms by far the largest part of the whole supply. A sweetened condensed milk generally contains rather more added cane-sugar than milk-solids. The following figures are typical of a good specimen:

Fat	11·0 per cent.
Proteins	10·0 ,,
Milk-sugar	14·0 ,,
Ash	2·2 ,,
Cane-sugar	38·0 ,,

3. The sweetened partly-skimmed class seems now to have almost disappeared.

4. Separated milks (generally 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 the practice.

The Sale of Food and Drugs Act, 1899, Sec. 11, made it compulsory to label condensed separated milk and condensed skimmed milk. The labels on some of the tins of inferior condensed milk bear the words 'skimmed,' but in such small type that the intimation might be easily overlooked. It should be made compulsory to add, 'Skimmed milk is unfit for the nourishment of children.' This recommendation has in effect been adopted in Hong-Kong (1911), Jamaica (1908), Australia (1912), and British Guiana (1913).

The following analyses are from a paper on 'The Composition and Analysis of Condensed Milk,' by T. H. Pearmain and C. G. Moor (*Analyst*, December, 1895), which contained the results on practically all the brands which were then on the market:

Brand.	*Total Solids.*	*Fat.*	*Milk-sugar.*	*Pro-teins.*	*Cane-sugar.*	*Remarks.*
	%	%	%	%	%	
First Swiss ..	36·7	10·5	14·2	9·7	—	Un-sweet-ened.
Ideal	38·0	12·4	16·0	8·3	—	
Viking.. ..	34·2	10·0	13·3	9·0	—	
Anglo-Swiss ..	74·4	10·8	16·0	8·8	37·1	Sweet-ened whole milk.
Fourpenny ..	76·5	10·4	13·0	9·8	41·3	
Mother ..	72·0	8·8	13·7	7·3	40·5	
Milkmaid ..	76·3	11·0	14·6	9·7	38·7	
Nestlé's ..	77·2	13·7	15·0	9·7	37·2	
Calf	58·0	1·0	16·0	7·5	31·9	Sweet-ened skim milk.
Cup	56·9	1·0	15·4	8·5	30·4	
Goat	71·0	1·2	12·0	9·9	45·9	
Handy ..	75·5	0·3	17·0	12·3	44·3	
Lancer ..	67·6	0·3	16·6	12·3	35·8	
Minstrel ..	75·3	0·2	15·4	9·7	48·3	

The Analysis of Condensed Milk.—The analysis of condensed milk should comprise estimations of the total solids, ash, proteins, milk-sugar, and fat. We have examined the ash of a number of milks for tin and lead, but they have been absent in every case.

In examining any tinned article for tin or lead, great care must be taken to use a *sharp* tin-opener, or fragments of metal may be torn off and vitiate the result. The tin should be cut open; the contents should be thoroughly mixed.

It is sometimes a matter of considerable difficulty, if not an actual impossibility, to render the contents of a tin perfectly homogeneous. Macfarlane (*Canadian Bulletin*, No. 69) points out that milk-sugar sometimes forms an almost invisible crystalline deposit, which is very difficult again to incorporate evenly throughout the viscid mass. Portions taken from different parts of the same tin, even after it has apparently been thoroughly mixed, give divergences of results that cannot be accounted for by experimental error.

Unsweetened condensed milk may be analysed by adding to a convenient weight of it twice its weight of water, raising just to the boil, and using the ordinary methods of milk analysis.

In the case of a sweetened condensed milk it was shown by Otto Hehner in 1879 that the presence of cane-sugar interferes to a considerable extent with the extraction of the fat.

The following scheme will be found convenient for the analysis: 10 grammes are made up to 100 c.c. This 10 per cent. solution serves conveniently for the following estimations:

Total Solids. — Twenty c.c. of the solution are evaporated in a platinum dish and dried in water-oven till constant in weight; this will take five or six hours.

Ash.—The same quantity will serve for the determination of ash, and should be ignited at as low a temperature as possible. The ash in condensed milk varies, but on the average is somewhat over 2 per cent.

Proteins.—The nitrogen is determined on 10 c.c. of the solution by the Kjeldahl process; the proteins are then calculated by the 6·38 factor.

Richmond and Boseley (*Analyst*, May, 1893) give methods for the estimation of the casein and the albumin, and point out some of the errors liable to

occur in the use of Ritthausen's process for determining proteins.

Milk-Sugar.—This may be estimated by one of the Fehling processes. This constituent being required in terms of anhydrous lactose, the Fehling's solution should be standardised (if a volumetric process is selected) or the results checked (if a gravimetric process is done) against anhydrous lactose. The latter is obtained by evaporation of a pure lactose solution.

J. Bristowe P. Harrison (*Analyst*, 1904, p. 248) discusses the estimation of the lactose and cane-sugar by polarimetric methods. Revis and Payne (*Analyst*, 1914, p. 476) use acid mercuric nitrate both as clarifying agent and inverting agent. They also give corrected inversion factors in the Clerget formula.

Cane-Sugar.—In the case of sweetened condensed milks it is usual to subtract the sum of the ash, fat, proteins, and milk-sugar from the total solids, and to consider the difference added sugar. If an estimation is needed, advantage is taken of its inversion by citric acid, which does not invert lactose.

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. The Gottlieb process is very satisfactory, especially for sweetened condensed milks.

The Werner-Schmid process is inapplicable to sweetened condensed milk owing to the charring of the cane-sugar, which renders a satisfactory extraction of the fat impossible. The Gerber process gives a comparatively accurate figure, but it should be given two or even three whirlings in order to get out all the fat, and it is obvious that a stronger solution of the milk than 1 in 10 must be used.

Revis and Payne (*Analyst*, 1914, p. 479) say that in any well-made condensed milk the true percentage of lactose can be calculated with a fair degree of accuracy as being $\frac{3}{4}$ths of the non-fatty milk-solids present. With sweetened milk a useful variant (when no protein has been added) is that $\frac{3}{9}$ of the protein will give an approximate figure for lactose.

After prolonged storage in the tropics, some brands of sweetened condensed milk develop a brown colour

and increase in consistency. Colonel W. W. O. Beveridge (*Journ. R.A.M.C.*, 1914, January) finds these to be the results of an acid fermentation of the proteins by spore-bearing bacilli, the colour being presumably due to the production of reducing sugars, especially from the cane-sugar.

Attempts have been made to replace the fat in separated condensed milk by foreign oil or fat. This would be detected by extracting 200 grammes of the sample with ether, after grinding with enough anhydrous sulphate of copper to form a dry powder, and examining the fat when quite free from the solvent by the tests described for butter.

*A sample of condensed milk may be regarded as genuine which fulfils the following requirements :**

1. The fat must not be less than 10 per cent., and must be true butter-fat.

2. The proteins, estimated by multiplying the nitrogen figure by the 6·38 factor, must not exceed the figure obtained for fat.

3. The sample must be free from preservatives (except sugar), starch, and all other foreign matters.

BUTTER.

By continuously shaking or beating milk at a high temperature, the fat corpuscles can be divided and their number increased. If, however, the milk is cooled, and is then shaken or beaten, the fat corpuscles adhere together and form *butter*, a thin bluish *butter-milk* remaining behind.

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 native colour is principally carotin. There appears to be no means of distinguishing between natural and added carotin. The colour fades on prolonged exposure to light.

* This standard was suggested in 'Milk and Milk Products' (T. H. Pearmain and C. G. Moor, 1897), and is identical with that proposed by the Departmental Committee in their Report of 1901.

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.' Small amounts of lauric acid, arachidic acid, and dioxystearic acid triglycerides are also present (Hammarsten).

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

Butyric acid	6·1 per cent.
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 has been determined by Chevreul, Benedict, and Zsigmondy, and by Allen, who obtained figures varying from 10·2 to 11·85 per cent.

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

Tributyrin Tripalmitin Triolein
$C_3H_5(O.C_4H_7O)_3$ $C_3H_5(O.C_{16}H_{31}O_3)$ $C_3H_5(O.C_{18}H_{33}O)_2$.

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 character:

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

On keeping, butter may turn rancid, especially it the butter-milk has not been properly washed out; but such decomposition as the butter would undergo in the course of two or three months would probably never be sufficient to invalidate the Reichert or Valenta figures.

Butter is adulterated by substituting foreign fats, such as coconut oil and margarine, and by the incorporation of excessive amounts of water, salt, or preservatives. Casein and starch have also been added, the former as a scientific adulterant, and the latter probably as a drier.

Margarine.—Margarine is prepared by churning melted and clarified animal and vegetable fats, usually beef or mutton fat, occasionally lard, and cotton-seed, sesamé, palm-kernel, and coconut oils, with skim milk, milk, or cream; in this way the curd or casein found in the margarine acquires more or less the flavour of butter. When carefully prepared and coloured it is not easy to tell margarine from butter by taste or smell.

J. C. Drummond and W. D. Halliburton (*Journal of Physiology*, 1917, March 20) found oleo-oil margarine (*i.e.*, containing beef-fats) as satisfying as butter for the nutritive requirements of the young rat. Margarines and lard substitutes composed of vegetable fats did not enable the young rat to grow to adult size, with the exception of a preparation containing crushed coconut fibre, which contains a fat-soluble accessory substance not present in the expressed oil. The experiments, unfinished though they be, form striking commentary on the frequently expressed opinion that 'margarine is as good as butter.'

The Sale of Food and Drugs Act, 1899, Sec. 8, limits the amount of butter-fat in the fat of margarine to 10 per cent. This is a larger proportion than is allowed in imported margarine by the Butter and Margarine Act, 1907, Sec. 5, which fixed the limit for butter-fat *in margarine* at 10 per cent.

The Butter and Margarine Act, 1907, restricts the amount of water to 16 per cent. The Act defines margarine as 'any article of food, whether mixed with butter or not, which resembles butter and is

not milk-blended butter.' In Germany it is obligatory for margarine manufacturers to add 10 per cent. of sesamé oil to their product to facilitate detection; a proposal to make the same addition compulsory in this country was adduced by the Departmental Committee on Butter Regulations. In some foreign countries the addition of colouring matter to margarine is forbidden. Conversely, an Australian Customs Regulation prescribes a distinct pink colour to be imparted by the admixture of alkanet root.

Starch has been found in margarine by Arnaud and other analysts to the extent of about 2 per cent. Although the samples contained about 26 per cent. of water, they did not appear 'wet.' In Queensland (1910) starch is ordered to be added for the purpose of earmarking it.

Hydrogenated fats and oils yield emulsions containing more water than ordinary fats and oils do, and when made into margarine, it is said to be not unusual for the latter to contain 20 per cent. of water (*Analyst*, 1917, p. 49).

Paraffin wax has been added to margarine to improve consistency and texture.

Any fictitious butter can 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 yielding only traces of 'soluble' fatty acids. It consists mainly of the glycerides of oleic, stearic, and palmitic acids. The absence of glyceryl butyrate, 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 Kirschner tests.

Calculation of the percentages of the constituent fats is often a difficult matter, margarine fat being frequently of a complex nature. Practically any of the determinations and identifications used in the analysis of fats may be required.

The Analysis of Butter.

Water.—Good quality dairy butter contains about 12 per cent. of water; Siberian butter contains less than this, and factory butter about 15 or 16 per cent. The Butter Regulations, 1902, and the Butter and Margarine Act, 1907, fixed a standard of 16 per cent. of water. This standard of 16 per cent. was suggested in the first edition of this book (T. H. Pearmain and C. G. Moor, September, 1895). The same Act fixes a standard of 24 per cent. of water for milk-blended butter, and such butters may only be designated by names approved by the Board of Agriculture. The presence of so much water interferes with the keeping qualities of the butters, and they will generally be found to contain a preservative.

The 16 per cent. limit for water in butter has been adopted in Australia (1912), Cape of Good Hope (1914), Natal (1914), Canada (1914), and virtually in Sweden too. We have made a practice for some years of averaging the water we found in butters containing preservative and comparing it with the average water in butters free from preservative. We find the former consistently higher (in some years by as much as 2 per cent.) than the latter, and we should not be surprised if preservatives were much less frequent were a lower maximum for moisture prescribed.

To estimate the water, a platinum dish containing a piece of platinum wire is weighed, and then 10 grammes of butter are weighed into the dish. The dish is carefully heated over a small flame (the butter being stirred constantly with the platinum wire), until the crackling noise due to the evolution of the water has ceased and the casein takes a brown tint. The dish is allowed to cool, and then weighed, and the difference in weight multiplied by 10 gives the percentage of water in the butter. The platinum wire may be dispensed with and the water driven off by gently rotating the dish, held in with crucible tongs, high over a flame, care being taken that no butter is lost by 'spitting' or by getting on the

tongs; or the water may be estimated by weighing a small quantity (2 grammes) into a flat-bottom dish, melting the butter in the water-oven, and then adding 1·5 c.c. of absolute alcohol, which is mixed with the fat. The dish is replaced in the water-oven until the weight is constant.

It often happens that butter is received for analysis in a jar with a portion of the water exuded. In such cases a fairly accurate determination of the water can be made if the sample is cautiously and very slowly warmed in a water-oven till it shows sign of incipient melting, when it is well worked with wide and flexible spatula. A little moisture is sure to be lost while reworking the mass, and the determination should be done in triplicate to prove that homogeneity was attained.

Salt.—The residue, after burning off the fat from the above, can be taken as salt for all practical purposes. The salt may amount to, but does not often reach, 10 per cent.

There is no standard for salt in this country, but not more than 4 per cent. is permitted in butter in Australia (1913), Cape of Good Hope (1914), and Natal (1914). McGill regards 6 per cent. as the highest amount of salt to be tolerated by the palate.

Casein, or **Curd,** can be estimated by expelling the water as directed above, and washing the residue with ether till free from fat. Casein and salt are left. The casein varies from 0·3 to 1·9 per cent.

A limit of not more than 3 per cent. of casein is adopted in Australia (1913). The proteins in butter can be estimated with a fair degree of accuracy by a determination of the aldehyde figure (*Analyst*, 1912, p. 50).

Examination of Fat.—The sample is put into a beaker and placed in the water-oven. The curd and water will generally separate, leaving the fat bright. The fat is then decanted and filtered through a dry filter. The fat should be quite clear and bright.

The fat is now examined by the Reichert-Wollny process, the Polenské process, and by the Valenta test, or the Zeiss butyro-refractometer. The indications

given by these tests are generally all that is necessary, but in cases of suspicious or adulterated samples it may be desirable to determine the Kirschner value and the Avé Lallement values, in addition to qualitative tests for possible adulterants. In fact, nearly all of the tests described for fat and oil analysis may on occasion be required in an attempt to identify and estimate adulterants when only present in comparatively small amounts.

The Reichert-Wollny Process for the Estimation of the Volatile Fatty Acids.—The following description is that agreed to by the Government Laboratory and the Society of Public Analysts: 5 grammes of the liquid fat are introduced into a 300 c.c. flask (length of neck 7 to 8 centimetres, width of neck 2 centimetres). Two c.c. of a solution of caustic soda (98 per cent.) in an equal weight of water—preserved from the action of atmospheric carbonic acid—and 10 c.c. of alcohol (about 92 per cent.) are added, and the mixture is heated under a reflux condenser connected with the flask by a T-piece, for fifteen minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot distilled water, which have been kept boiling for at least ten minutes, are added, and the flask shaken until the soap is dissolved. Forty c.c. of normal sulphuric acid, and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 millimetres wide and 15 centimetres from the top of the cork to the bend. At a distance of 5 centimetres above the cork is a bulb, 5 centimetres in diameter. The flask is supported on a circular piece of asbestos 12 centimetres in diameter, having a hole in the centre 5 centimetres in diameter, and is first heated by a very small flame, to fuse the insoluble fatty acids, but the heat must not be sufficient to cause the liquid to boil. The heat is increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting about thirty minutes (say from twenty-eight to thirty-two

minutes); the distillate is shaken, 100 c.c. filtered off, transferred to a beaker, 0·5 c.c. of phenolphthalein solution (1 gramme in 100 c.c. alcohol) added, and the filtrate titrated with decinormal soda or baryta solution. Precisely the same procedure (with the same reagents), omitting the fat, should be followed, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained by blank experiment, is multiplied by 1·1. The number so obtained is the Reichert-Wollny number.

Notes on the Method.—The Soxhlet spherical condenser is a convenient one for the reflux distillation. This is fixed near the water-bath in which saponification is to take place, and is connected with the flask by means of a **T**-piece and indiarubber tubes inclined at an angle of 45 degrees. During the saponification the free limb of the **T**-piece is directed upwards, and its end closed by a short piece of indiarubber and glass rod. At the end of fifteen minutes this limb is turned downwards, and the piece of glass rod replaced by a tube carrying away the alcohol. A Liebig condenser containing a column of water 30 to 35 centimetres in length gives sufficient condensing surface. After shaking the distillate, about 5 c.c. are filtered through dry paper into a 100 c.c. flask. This serves to wash out the flask. When the 100 c.c. are transferred to a beaker the flask is not washed out, but the main quantity is neutralised with the standard solution of alkali and returned to the flask, then again transferred to the beaker, and the titration completed. The Committee adopted a Reichert-Wollny number of 4 as representing 10 per cent. of butter-fat when margarine is under examination. (If much coconut oil be present, the Reichert-Wollny number of 4 may be exceeded without more than 10 per cent. of butter-fat being present.) Genuine butter-fat gives Reichert-Wollny numbers from 24 to 32. The Butter Regulations Committee recommended that a Reichert-Wollny figure of 24 be taken as the limit for butter. This figure was not reached by 42 examples out of 1,037 examined in the Govern-

ment Laboratory in 1916, but 24 of these exceptions came over 23. Irish butter produced in winter, Russian and Siberian butters, occasionally fall below 24.

Coconut oil gives a Reichert-Wollny number of 7. Palm-nut (palm-kernel) fat gives a figure about 5, while certain fish oils give values above 40. These last would, however, be improbable adulterants of butter.

Glycerol may be used instead of alcohol for the saponification of the butter-fat, and this substitution is necessary when a Polenské figure is required (see below).

Towards the end of the lactation period there is a distinct fall in the Reichert-Wollny number, which increases after calving. Benzoic acid, when added as a preservative, increases the Reichert figure, being carried over in the steam. In the usual proportions in which it is used (0·1 to 0·2 per cent.), the influence of benzoic acid is insignificant. Salicylic acid has the same effect to a smaller degree.

The **Polenské Method** (*Analyst*, 1904, p. 154) is based on a determination of the insoluble volatile fatty acids that come over in the Reichert process. Certain arbitrary conditions as to dimensions of the apparatus and experimental conditions must be adhered to.

Five grammes of the fat, 20 grammes of glycerol, and 2 c.c. of 50 per cent. sodium hydroxide solution are heated over a naked flame, with constant shaking, until a clear solution is obtained. An alcoholic solution of sodium hydroxide as employed in the Reichert process must *not* be used. The soap is dissolved in 90 c.c. of hot water, 50 c.c. of approximately normal sulphuric acid, and 0·1 gramme of powdered pumice, which has been previously sifted through muslin, are added, and the flask is quickly connected to the top of an upright Liebig condenser by means of a glass tube with a bulb just above the cork, and bent first at an obtuse angle and then at an acute angle. The flame under the distillation-flask is so regulated that 110 c.c. of distillate are obtained in from nineteen to twenty-one minutes

When 110 c.c. of distillate have been collected, the distillate flask is replaced by a 25 c.c. cylinder to catch the drainings. Without mixing the contents the 110 c.c. flask is placed in a bath of water at 10° C. for ten minutes, the surface of the water in the bath being just above the 110 c.c. mark. The insoluble fatty acids are almost invariably of an opaque white character in the case of butter, while clear oily globules are present if coconut oil to the extent of over 10 per cent. be present. The contents of the distillate flask are now mixed and filtered, and the Reichert-Meissl figure may be obtained on the filtrate. The condenser, the 110 c.c. flask, and the cylinder are washed with 18 c.c. of water, which are poured over the filter. As sometimes described, directions are given to use three lots of water of 15 c.c. each, but the one wash of 18 c.c. is generally adopted and the difference is negligible. This filter, condenser, and cylinder, carry now all the insoluble volatile fatty acids which have come over in the process, and these are dissolved in alcohol and the solution titrated with decinormal barium hydrate, using phenolphthalein as an indicator. The number of cubic centimetres of the decinormal alkali required is termed the 'new butter value' of the fat.

Polenské found that the 'new butter figures' on genuine butter rose with the Reichert values, and varied from 1·3 for a butter with a Reichert figure of 20 to 3·0 for butters with a Reichert of 30. Each increase in the 'new butter value' of 0·1 c.c. corresponds to an addition of 1 per cent. of coconut fat.

Butter-fat from cows fed on coconut oil cake or beetroot leaves yields a Polenské figure exceeding the maximum figure for the corresponding Reichert-Meissl number (*Analyst*, 1911, p. 449; 1914, p. 254).

Coconut oil gives a Polenské value of 15·4 to 17·5 and palm-kernel oil one from 9 to 11.

Kirschner's Process. — This extension of the Reichert-Meissl process offers little advantage over the Polenské method for coconut oil in butter, but the opinion has been expressed that it will decide whether butter-fat is present in a margarine containing coconut oil, even if the amount be only 2 per

cent. in conjunction with 75 per cent. or more of coconut oil (Bolton, Richmond, and Revis, *Analyst*, 1912, p. 183).

The process (*Analyst*, 1905, p. 205) is as follows: 100 c.c. of the filtered distillate from the Reichert-Meissl process are titrated with decinormal barium hydroxide solution, to obtain the Reichert-Meissl value. To the neutral solution 0·5 gramme of silver sulphate is added, and the mixture shaken from time to time for one hour. The solution is then passed through a filter, and 100 c.c. of the filtrate transferred to a distillation-flask. After adding 35 c.c. of water, 10 c.c. of dilute sulphuric acid (1 : 40), and a few pieces of pumice-stone, the whole is distilled; 110 c.c. of distillate are collected, filtered, and 100 c.c. of the filtrate titrated with decinormal barium hydroxide solution. The number of c.c. of the latter required, calculated back to 5 grammes of fat, is termed the 'second titration' value. Kirschner worked out two formulæ for the amounts of butter-fat and coconut oil in margarine. The percentage of butter-fat = $4{\cdot}319\ S - 0{\cdot}456\ R - 2{\cdot}15$, and the percentage of coconut oil = $7{\cdot}42\ R - 8{\cdot}116\ S - 3{\cdot}57$, where S = the 'second titration' value and R = the Reichert-Meissl value of the sample.

The comparative values obtained by Bolton, Richmond, and Revis (*loc. cit.*) agree with those given by H. T. Cranfield (*Analyst*, 1915, p. 440) for butter:

Kirschner Value.	Limits of Polenské Value.
19–20	1·4–1·7
20–21	1·4–2·2
21–22	1·7–2·7
22–23	1·8–2·9
23–24	2·2–2·6

The Kirschner value is practically a measure of the butyric acid, and hence is likely to reach its maximum in butter and to be much smaller in butter adulterants. Bolton and Revis ('Fatty Foods') give values of 1·6 to 1·9 for coconut oil and 1·07 for palm-kernel oil.

Arnaud and Hawley (*Analyst*, 1912, p. 123) used the following equations for calculating the percentage of butter-fat in margarine:

$$K = (K' - 0{\cdot}5) - \frac{P}{10}.$$

In this, K = corrected Kirschner figure; K′ = Kirschner value found; P = Polenské value found, and the 0·5 is the Kirschner value they adopt for butter-free margarine. Then, percentage of butter-fat $= \frac{100\ K}{23}$.

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 (except coconut oil) do not form a clear mixture, except at a much higher temperature. The acetic acid used must be set against samples of butter-fat of known purity. If about 99 per cent., it will give a turbidity with genuine butter-fat at from 32° to 36° C. A weaker acid giving turbidity temperatures with butter-fat between 45° and 55° C. will serve equally well. With butter-fat, the turbidity temperature is principally dependent on the proportion of glyceryl butyrate. That is to say, as the turbidity temperature increases the Reichert-Wollny number decreases. Hence, for standardising the acetic acid, a butter-fat having a Reichert-Wollny number of about 28 should be selected. Then, the large majority of butter samples will give Valenta figures within 5° or 6° C. either way of that. The whole secret of the successful use of the test lies in the absence of moisture from all material and apparatus used, as addition of moisture raises the Valenta figure. Everything must be warm enough to prevent deposition of atmospheric moisture.

This test is carried out as follows: A test-tube is graduated by running two quantities of 3 c.c. of water from a burette or pipette; file scratches are made exactly opposite the dark line forming the meniscus. The tube is then dried thoroughly, and 3 c.c. each of the fat and acetic acid poured in cautiously and with gentle mixing till the contents of the

tube become clear. By stirring the mixture with a thermometer, the temperature can be noted as soon as the point of turbidity is reached. It makes its first appearance as a tail following the thermometer bulb. (See 'The Acetic Acid Test,' by Chattaway, Pearmain, and Moor, *Analyst*, 1894, p. 147.)

With acid giving a pure butter figure of 34°, an oleo-oil margarine fat will become turbid about 75° C. and coconut oil about 14° C. With a pure butter figure of 50°, an oleo-oil margarine may give figures from 90° to 100° C. and coconut oil about 20° C. There are on the market at present brands of margarine in which the proportions of coconut oil are so adjusted, perhaps inadvertently, perhaps not, that the fats give pure butter figures with this test. Such fats will also give Zeiss butyro-refractometer readings, and specific gravities within the respective pure butter ranges. While a margarine may give figures anywhere in the range from coconut oil to beef-fat, an abnormally low Valenta will not necessarily indicate coconut oil; a butter-fat giving a Reichert-Wollny number of 34, for example, would come below the tentative minimum of the 10° range found as above. Inasmuch as there is a longer scale of reading for edible fats, the Valenta has an advantage over the butyro-refractometer, and there is little doubt that more extended study of it will enhance its usefulness in some modified form. If the acetic acid, having congealed with cold, should require melting, the whole of the contents of the bottle should be melted, before using any; the first portion to liquefy is weakest in strength and may give higher figures than a representative portion of the acid.

The Determination of the Refractive Index (The Zeiss Butyro-Refractometer).—This instrument consists essentially of two prisms, between which the butter or substance to be tested is put, surrounded by water-jackets for keeping the prisms at the required temperature. A telescope containing an eyepiece and scale is attached, while the light for the leading is obtained by means of a mirror The

apparatus contains inlet and outlet for water and a thermometer. In the case of butter, observations are made at 35° C. or 40° C.

A special heating apparatus can be used for the supply of water at the requisite temperature, or a large vessel filled with water a few degrees above the required temperature, from which the water is siphoned by an indiarubber tube, can be used, and the flow of water so regulated by a screw clip that the requisite temperature can be obtained. Everything being ready for the experiment, the milled head opening the prisms is turned, the apparatus raised so that the lower prism is horizontal, and two or three drops of filtered melted butter are allowed to drop on the prism, which is then shut up. The mirror is arranged so as to reflect whatever light is used through the prisms, and when the temperature is satisfactory, an observation is made through the telescope. If the surface between the prisms be not uniformly filled with butter, the critical line will be indistinct. Instead of taking the reading at a constant temperature, this may be observed at any suitable temperature, and the reading corrected to the standard temperature, allowing a mean value of 0·55 scale division for each degree Centigrade, and adding or subtracting the result to or from the refractometer reading, according as to whether the temperature is higher or lower than the standard. Another thermometer supplied with the instrument, instead of registering the temperature, indicates the normal reading for butter-fat at that particular temperature, and also the normal reading for lard. A standard oil is provided for adjusting the scale.

It being difficult to remove all trace of the previous sample tested by wiping with a cloth alone, the surfaces should be smeared with some of the fat to be tested, which is wiped off and then more of it added for the actual test.

The fact that the thermometer will register a temperature earlier than the prisms could attain it, should not be overlooked, and, when starting a series of tests, the first sample should be read twice with an interval of five minutes.

At 35° C. butter gives figures varying from 44° to 49°, generally about 46°. A butter giving a reading above 47° should be regarded with suspicion. At the same temperature oleo-margarine gives about 54°, and coconut oil about 43°.

At 40° C. the usual range for butter-fat is 41° to 45° (narrow limits), and an additional degree either way for genuine, though less frequent, readings. Butter from cows fed on coconut cake may give figures below the normal, or if fed on linseed cake above the normal.

The following Zeiss readings are the results of observations by Bolton, Trimen, and ourselves. All are stated at 40° C.:

Coconut oil	34·3° to 35·5°
Palm-kernel oil	37°
Mutton-fat	47·2°
Oleo-oil (beef)	47·5° to 48·7°
Lard (narrow range)	49° to 51·2°
Lard (wide range)	48° to 52°
Cotton-seed oil	58·6°
Sesamé oil	59° to 61·6°

Other observations with this instrument are recorded in the chapter on 'Oils and Fats.'

The Specific Gravity of Butter-Fat.—The specific gravity at the ordinary temperature is now but seldom taken, it being more convenient to take it at the temperature of boiling water (98° to 100° C.), comparing it with water at 15·5° C. as unity.

A Sprengel tube is filled with the melted fat by sucking its contracted end, 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, margarine, and coconut oil at a temperature of about 99·5° C. compared with water at 15·5° C. taken as 1,000:

Butter-fat	.. ..	865·3 to 866·8
Margarine (oleo-oil)	..	856·0 to 860·0
Coconut oil	.. ..	868·0 to 872·0 (Mann)

Margarine giving Valenta figures and refractometer readings within the respective butter-fat ranges, will have specific gravities within the butter-fat range as well. The specific gravity of butter-fat apparently rises with the Reichert-Wollny number.

The **Koettstorfer Saponification Equivalent** of butter-fat varies from 242 to 253, the mean figure for oleo-oil margarine being about 284. For method, see ' Oils and Fats.'

The **Iodine Absorption** of butter-fat ranges from 23 to 38 per cent., oleo-oil margarine giving from 40 to 55 per cent. of iodine absorbed. For method, see ' Oils and Fats.'

Microscopical Examination of Butter.—Stokes uses the microscope with polarised light. He cuts a piece off the sample to obtain a clean surface; this surface is *lightly* scraped all along so as to get as representative a portion as possible. The scrapings should not measure more than about one-tenth of the size of an ordinary pea. This is transferred to a small cover-glass, which is then pressed down on to an ordinary microscopical slide, so that the butter lies in the form of a wedge between the two glasses, one side being pressed very thin, while the opposite side is left very thick. The slide thus prepared is placed under the 1-inch power of the microscope, which must be provided with a good polarising apparatus. The thinnest edge of the preparation should be so arranged that it cuts across the middle of the field of view, one-half of the field being left blank. Gas-light should be used.

On rotating the Nicol's prisms, so that the two prisms are at right angles, the whole of the field will

remain equally dark if the sample be pure butter. If, however, as much as 20 per cent. of margarine be present in the sample, it will be impossible, however the prisms may be placed, to darken the side of the field occupied by the sample. Margarine gives, when thus viewed, a similar appearance to that of a cloud in a dark sky.

No selenite plate should be used. The butter should not be melted. The test has its limitations. Richmond says that old butters, especially those which have been submitted to vibrations, and butters prepared by processes in which the cream has been churned soon after heating and cooling, may show a somewhat crystalline appearance.

Sesamé Oil is readily detected by Baudouin's test (see p. 212).

The addition of hydrochloric acid alone to butter-fat sometimes produces a pink colour owing to the presence of curcuma or a tar-dye, so that care must be taken not to put down to the presence of sesamé oil a colour due to a dye.

The butter from cows fed on sesamé-oil cake does not give a reaction either with Baudouin's or Soltsien's reagents.

Cotton-Seed Oil.—This is detected by Conroy's (the silver test) or Halphen's tests (see p. 215). One of us (C. G. M.) has shown that butter made from the milk of cows fed on cotton-seed cake gives an unmistakable darkening with Conroy's silver reagent.

Starch.—This may be detected by melting the sample in a small beaker, pouring off the fat, and adding a solution of iodine in potassium iodide. In a normal butter the curd and water give only a reddish coloration, while a very small trace of starch will give a blue liquid or grains. The curd, etc., may also be examined microscopically before and after the addition of iodine.

Coconut Oil.—The detection and estimation of this butter adulterant, which has come into use of recent years, necessitates the extension of the scheme of analysis. If the insoluble volatile fatty acids obtained in the distillate flask of the Reichert-Wollny process remain liquid when cooled to room tempera-

ture, coconut oil is very probably, but not necessarily, present. A low Valenta figure and a low butyro-refractometer reading would also suggest its presence. Coconut oil gives a Reichert-Wollny figure of 7; an iodine absorption figure of 9; a specific gravity at 99° C. (water at 15·5° C. = 1) of 0·866 to 0·875 (Southall's 1915 range); a melting-point of 24° to 26·5° C.; and a saponification value of 255 to 269. The Reichert-Wollny number compared with the Polenské figure and the Polenské figure compared with the Kirschner value (see *ante*) afford the best means of detecting and estimating it in butter. When palm-kernel oil is present as well as coconut oil, estimation of the separate proportions is somewhat hopeless, but the work of Burnett and Revis (*Analyst*, 1913, p. 255) may be of assistance.

E. Hinks (*Analyst*, 1907, p. 160) has devised a microscopical method, which, in expert hands, affords every satisfaction. The method requires a cold stage, and it is only after considerable experience that the typical crystals can be obtained and identified.

The phytosterol acetate test affords a certain means of detecting coconut oil or any vegetable oil when present to the extent of 10 per cent.; but as it requires 100 grammes of butter, it is but seldom that it can be applied. Coconut oil yields 0·09 to 0·30 per cent. of crude phytosterol and the melting-point of its acetate was 122 to 125° C. (*Analyst*, 1912, p. 497).

Other Adulterants.—A magnesium salt has been used to enable the butter to retain excessive moisture without showing it. Cane-sugar and dried milk have also been added. Dried milk can be detected by the increase in lactose, which in butter does not usually exceed 0·4 per cent., though amounts up to 1 per cent. have been found. It is used for renovating butter, and is found more easily used as a 'starter' than milk.

Colouring Matter in Butter.—Artificial colouring matters, such as annatto, turmeric, saffron, saffronette, marigold, and the azo-dyes, are very frequently added to butter. Such addition is not regarded as an adulteration in this country. It should be noted

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.

Sprinkmeyer and Wagner (*Analyst*, 1905, p. 244) give a method which is said to detect all the ordinary butter colours. Ten c.c. of the melted fat are placed in a separating funnel, and dissolved in 10 c.c. of light petroleum. When this solution is shaken with 15 c.c. of glacial acetic acid, the presence of foreign colouring matter is shown by the lower (acetic acid) layer becoming yellow or red in colour, the red coloration being produced by alizarine and aniline yellows and by tropæolin. (See also a scheme in *Analyst*, 1908, p. 421.)

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

Preservatives in Butter.—A considerable amount of butter is made from pasteurised cream with a pure starter. This is the best method of delaying decomposition. A low amount of water in the butter also conduces to its preservation. Chemicals are, however, extensively used, boron compounds being the most popular, although saltpetre, benzoic acid, formaldehyde, and boro-fluorides are likewise employed. Since so great a quantity as 10 per cent. of salt is necessary for preservative action, this compound is but seldom employed alone for the purpose.

The Departmental Committee on Preservatives and Colouring Matters, 1901, recommended 'that the only preservative permitted to be used in butter and margarine be boric acid, or mixtures of boric acid and borax, to be used in proportions not exceeding 0·5 per cent. expressed as boric acid.' That they would have been well advised to have added a recommendation that butter so preserved should be labelled, will be seen from the fact that a person eating about 2 ounces of butter containing ½ per cent. of boric acid is taking the lower Pharmacopœial dose of boric

acid (5 grains). Were butter so preserved labelled, the purchaser could refuse such butter if he desired.

Boric Acid may be detected in the ash by the method given under 'Milk.' It is best estimated by Richmond and Harrison's process: 25 grammes of the butter are weighed in a beaker, and to this are added 25 c.c. of a solution containing 6 grammes of milk-sugar and 4 c.c. of normal sulphuric acid in 100 c.c. The beaker is placed in the water-oven until the fat is just melted, when the whole is well mixed by stirring. After allowing the aqueous portion to settle, 20 c.c. of this portion are pipetted off, a few drops of phenolphthalein solution added, and the contents of the beaker are brought to the boil. Semi-normal sodium hydroxide solution is run in till a faint pink colour appears, the amount of alkali run in being disregarded. Twelve c.c. of glycerol are then added, when the pink colour disappears, owing to the liberation of boric acid, and the semi-normal soda is again run in till the faint pink colour reappears. The number of cubic centimetres of soda run in subsequent to the addition of the glycerol is noted, and when multiplied by 0·0368 gives the amount of boric acid in the 20 c.c. of aqueous liquid drawn off. The aqueous liquid is produced not only by the 25 c.c. of milk-sugar solution added, but also by the amount of water in the butter; thus, if the butter contains 12 per cent. of water, our aqueous liquid contains 25 + 3 c.c. (the water in 25 grammes of butter) = 28 c.c. The amount of boric acid in the 20 c.c. of aqueous liquid should, therefore, be multiplied by

$$\frac{100 + \text{percentage of water in the butter}}{20},$$

which will give the percentage of boric acid in the sample.

Benzoic Acid is sometimes used alone as a butter preservative, sometimes with borates, and occasionally with fluorides. Benzoic acid may be detected by the process given under 'Milk.'

Salicylic Acid may be estimated by the method used in the Paris Municipal Laboratory: 20 grammes

of the sample are repeatedly exhausted by a solution of bicarbonate of soda, which converts the salicylic acid into the soluble sodium salicylate. The aqueous liquid is acidulated with dilute H_2SO_4, and extracted with ether; on the addition of a little mercurous nitrate to the residue after evaporating off the ether, 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 is diluted with an equal volume of 95 per cent. alcohol, and titrated with $\frac{N}{10}$ alkali, using phenolphthalein as indicator (1 c.c. 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.

Fluorides.—Hehner (*Analyst*, 1902, p. 171) gives the following process for the detection of fluorine, which will detect 1 milligramme of calcium or sodium fluoride: The boron compounds have first to be eliminated. The aqueous liquid is separated from 50 grammes of the butter, and without clarifying it calcium chloride is added, the liquid heated to boiling, and a small excess of sodium carbonate added to precipitate the calcium compounds. The precipitate is filtered off, ignited, and treated with hot dilute acetic acid, which dissolves out the carbonate, borate, and phosphate. The residue is again filtered, ignited, and transferred to a platinum dish, strong sulphuric acid added, and the dish covered with a slip of glass coated with beeswax on which a distinguishing mark has been scratched with a pin. (A pointed piece of wood or ivory is better than a pin, which is liable to scratch some forms of glass.) The dish is then heated on a sand-bath for two hours, and the glass slip is examined after the beeswax has been melted and wiped off, when distinct etching of the glass will be observed.

As a routine test Monier-Williams (L.G.B. Food Reports, No. 17) suggests the following, which is capable of detecting 0·1 per cent. of sodium fluoride or silico-fluoride in butter or margarine: 10 grammes of the sample are melted and shaken up in a separating funnel with ether and 1 or 2 c.c. of water. The aqueous layer is run off into a test-tube, a few drops of hydrogen peroxide added, and 1 c.c. of a solution containing about 2 per cent. of titanium sulphate in 10 per cent. sulphuric acid. A blank test is made in exactly the same way on 10 grammes of pure butter or margarine. If the original sample contained fluorine, the orange-yellow colour of the peroxidised titanium solution will be partially discharged. This is seen on comparison with the colour obtained in the blank test on pure butter. A positive test will need confirmation by the etching test, and its usefulness appears at present to be limited to butter and margarine.

All the evidence at present available stamps the use of fluorides as preservatives as an abominable practice. Even in small doses they have been shown to have deleterious effects on bone and blood.

Renovated Butter.—Butter which, owing to its rancidity, to the presence of moulds, or to bad preparation, is unfit for use, is sometimes melted, the water and curd removed, and the fat then aerated by air being blown through it. Fresh or dried milk inoculated with a bacterial culture is added, and the butter is chilled, granulated, churned, and prepared for market. When examined by polarised light renovated butter gives a blue field, mottled with yellow; it also gives a low Valenta figure and when cooled in milk in the Waterhouse test, it does not emulsify like butter or clot like margarine, but granulates and adheres to the wooden rod with which it is stirred.

CHEESE.

American Cheese is a Cheddar cheese, and usually contains about 33·0 per cent. of fat.

Caerphilly Cheese.—In 1911 the British Dairy Farmers' Association supported the Glamorganshire Chamber of Agriculture in the opinion that 'Caerphilly cheese was, is, and should be a whole-milk cheese.'

Camembert (France) is usually kept two months before being eaten. The ripening is effected by moulds. The cheese contains indole (Nelson).

Cheddar is the typical cheese of English manufacture.

Cheshire Cheese.—W. F. Lowe found the fat in twenty-six authenticated samples to range from 20·70 to 36·77 per cent. The Cheshire County Council suggested cheese sold as Cheshire cheese ought to contain at least 20 per cent. of fat. This was upheld by the Knutsford magistrates.

Cream Cheese may be made either by coagulating the cream with rennet, or by allowing it to sour naturally; it should contain about 40 per cent. of butter-fat (Cribb, *Analyst*, 1909, p. 45).

Dutch Cheese is prepared from milk partly deprived of fat, and in some cases from separated milk. Cribb (*Analyst*, 1906, p. 105) gives some analyses of Dutch cheese in which the fat varied from 1·64 to 27·9 per cent. He remarks the price increasing with the percentage of fat.

Gouda Cheese is said to be still made from whole milk, while **Edam Cheese** is now made from a mixture of the partly skimmed evening milk and the whole morning milk (*Analyst*, 1915, p. 391). Van Rijn says that cheese containing on the water-free substance less than 45 per cent. of fat may not be sold with the Government (Dutch) control mark.

Gloucester Cheese.—Two varieties are made: Single Gloucester and Double Gloucester. The distinction is one of size.

Gorgonzola when ripe is permeated by moulds, introduced by adding in the process of manufacture

powdered bread-crusts carrying moulds. Gorgonzola cheese is sometimes heavily coated with an artificial rind composed of barium sulphate, coloured pink with oxide of iron, and made up with some fatty material such as tallow. The rind may attain a thickness of $\frac{1}{4}$ inch, and E. Hinks (*Analyst*, 1911, p. 61) found it to vary from 16 to 27 per cent. of the whole weight of the cheese. As plugs of barytes may run $\frac{5}{8}$ inch into the cheese, some is likely to be eaten.

Gruyère comprises two hard Swiss cheeses prepared from cow's milk. Much of the cheese sold in England as Gruyère is known as Emmenthaler in Switzerland.

Parmesan Cheese is prepared from partly skimmed goat's milk.

Roquefort Cheese is prepared from partly skimmed ewe's milk. A. W. Dox found the small white specks sometimes to be observed in the cracks and crevices of Roquefort cheese to be crystals of tyrosine. He remarks on the high percentage of sodium chloride (3·64 to 4·50) present, which distinguishes it from Gorgonzola (1·57 per cent.) and Stilton (0·59 per cent.).

Skim-Milk Cheese is prepared either by natural souring or by the use of rennet.

Stilton is prepared from a mixture of whole milk and cream, or from whole milk alone.

The analyses of typical cheeses found on p. 87 were made by Pearmain and Moor (*Analyst*, July, 1894). No. 6 American cheese is a margarine cheese, and was bought by the vendor as genuine cheese.

The Board of Agriculture (*Annual Report*, 1913) think that Stilton and Wensleydale cheeses should be made either from whole milk or from whole milk and cream, and Cheddar, Cheshire, Cotherstone, Derbyshire, Lancashire, and Leicestershire, from whole milk, except, perhaps, towards the end of the season in certain cases.

In cheese made from whole milk the fat figure divided by the casein figure varies between 1 and 1·5 (Vieth). The New York State Dairy Commission's

Analyses of Various Commercial Cheeses.

	Name of Sample.	*Water.*	*Ash.*	*Fat.*	*Reichert Number.*	*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

experiments gave the ratio of 1 to 1·4 for cheeses made from whole milk, while those made from partially skimmed milk gave a ratio of 1 to 1·22.

The following figures were obtained by one of us on imitations of foreign cheeses made in England

under the auspices of the British Dairy Farmers' Association:

	Fat.	*Water.*	*Ash.*	*Nitrogen.*	*Proteins.* 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

Adulteration of Cheese.—Adulteration sometimes takes the form of the substitution of foreign fats for butter-fat, such cheeses being known as margarine or 'filled' cheeses: Skim milk is churned up with an emulsion of clarified animal or vegetable fats, and the mixture is curdled, pressed, and treated in the ordinary way. The sale of this product as 'cheese,' without any qualifying description, is an offence under the Food and Drugs Act, and little margarine cheese is found in this country.

The Sale of Food and Drugs Act, 1899, Sec. 5, extended the provisions of the Margarine Act so that it applied to margarine cheese. Italian regulations (1912) provide that margarine cheese shall be coloured over the whole of the external surface with the aniline colour known in commerce as 'victoria scarlet red.'

In some parts of England cheap cheese is found containing a minimum of fat (E. M. Hawkins found 1·68 per cent. in one) and loaded with water (up to 59·8 per cent.).

Standard for Cheese.—There being no standard for cheese in this country, cheese containing only traces of fat may be sold as cheese without any qualification.

When a standard for cheese is adopted, the following would be fair: not less than 30 per cent. of butter-fat, while no starch or other extraneous matter should be present. Any cheese not up to this standard should be required to be plainly marked, and sold as 'prepared from milk from which a portion

of the fat has been removed.' A higher standard—40 per cent. of fat—should be fixed for cream cheese.

At present 'cream cheese' need not even be a milk cheese, and if cream cheese is desired, it must be asked for as 'double cream,' or under some fancy name.

In the Cape of Good Hope (1914), Natal (1914), and Western Australia (1913), the standards for milk-fat in cheese are stated on the water-free substance. The first two require not less than 40 per cent., and the last 45 per cent. Western Australia has in addition standards for fat in skim-milk cheese (not less than 10 per cent.) and cream cheese (not less than 60 per cent.).

The Analysis of Cheese.

Water is estimated by drying 5 grammes of the sample in thin slices at a temperature of 100° C. till constant in weight.

The ash is estimated on the above by igniting at as low a temperature as possible. It will vary very largely (without taking into consideration the added salt) according to the amount of acidity that was permitted in the process of manufacture; the higher the acidity, the more calcium salts will have been dissolved and run off with the whey.

The proteins are obtained by multiplying the nitrogen figure by the factor 6·38.

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

Mechanical Process.—The fat can be determined by the following modification of the Leffmann-Beam process (p. 21):

Two grammes of the cheese, reduced to as fine a state of division as possible, are transferred to a small dish and treated on the water-bath with 15 c.c. concentrated hydrochloric acid until dissolved. The mixture is then poured into a Leffmann-Beam bottle, the dish rinsed with 3 c.c. of the HCl-fusel-oil mixture into the bottle, and, finally, enough hot strong HCl is added to fill the bottle to about the zero mark. It is then centrifuged for one minute. Readings multiplied by 7·77 give percentages of fat.

With Gerber bottles, 10 c.c. of sulphuric acid, 9·3 c.c. water, and 1 c.c. amyl alcohol, could be used, and readings be multiplied by 5·61.

When the amount of fat is small, the most accurate method is practically a modification of the Werner-Schmid method. Two grammes of the cheese are heated in a Werner-Schmid tube with 8 c.c. of water, then 10 c.c. of hydrochloric acid are added, and the tube is heated till the casein is destroyed, when, after cooling, the fat is extracted with ether, as in the Werner-Schmid process (p. 27).

To obtain fat for further work, it is generally sufficient to suspend about 50 grammes of the sample in a muslin bag in a beaker, and place in the water-bath; the fat will generally run out clear. The fat from the remainder of the ether in the process already given can also be obtained by evaporation.

The fat should be examined by the processes described under 'Butter.'

A cheese-fat will generally be found to give a lower Valenta figure than a butter-fat.

Starch.—A portion of the fat-free residue is boiled with water, filtered, and a dilute solution of iodine in potassium iodide added to the filtrate. No blue coloration should be obtained.

Saprophytes.—Cheeses, especially the moister kinds, are liable to the attacks of small insects and moulds. The principal animal organisms are the *cheese maggot* (the larva of a fly, *Piophila casei*) and the *cheese mite* (*Acarus domesticus*). 'Red mould' is caused by the fungus *Sporendonema casei*. *Aspergillus glaucus*, *Mucor mucedo*, and other moulds are sometimes found on cheese.

Poisonous Metals.—To preserve cheeses from the attacks of such organisms as those mentioned above, they are sometimes treated on the outside with antiseptics, occasionally of a poisonous nature, such as lead chromate, arsenious acid, and copper sulphate. 'Cheese spice' composed of sulphate of zinc has been used to prevent the cracking and heaving of cheese, and ferrous sulphide has been found in a Parmesan cheese. Allen and Hudson Cox state that the green mould in certain kinds of cheese has been imitated by the insertion of copper and brass skewers.

The ingestion of cheese may give rise to toxic symptoms owing to the presence of toxalbumins and tyrotoxicon.

STARCH FOODS.

The Microscopical Characters of the Starches.—For convenience of comparison we deal with the microscopical characters of the staple food starches together.

To examine starches under the microscope, the specimen should be mixed with a little cold water; a drop should then be placed on the slide, and a cover-glass superimposed. It should be examined, first with a $\frac{2}{3}$-inch, then with a $\frac{1}{6}$-inch, objective—the first to get a general view of the field, the second to examine individual granules. Fairly permanent preparations may be made by setting up in a drop of warm glycerin jelly, and ringing the slide in the ordinary way with Japan black.

The following descriptions must not be taken as characteristic of *all* the granules of a particular starch, as a number of granules diverge from the characters described, but by far the larger number conform to them. Where an estimation of foreign starch is necessary, several slides should be made up, and a count of typical granules made. When a rough estimate of the percentages has thus been obtained, a control specimen containing similar amounts of the starches should be made up and compared with the sample, and if this shows the

original judgment to be inaccurate, fresh specimens must be made up till the counts on sample and control agree.

The starches fall into five classes, according to their shapes: (1) Round—wheat, barley, and rye; (2) oval —pea and bean; (3) ovoid—potato and arrowroot; (4) semi-faceted—sago and tapioca; and (5) faceted—maize, oats, and rice.

Wheat, barley, and rye are all large round granules of a similar size; striæ are generally not visible; but while no hilum is visible in wheat and barley except under a high power, there is generally a well-marked stellate hilum in rye, and the latter granules generally show cracked edges. While wheat is characterised by having two sizes of granules, a large and a small, with but few intermediate sizes, barley shows more 'intermediary' sizes, and the small granules are smaller than the corresponding ones in wheat. Rye-flour is darker in colour than wheat-flour.

Pea, bean, and lentil starches are all oval granules, with faint concentric striæ and longitudinal hila, which often appear as irregular slits. It is difficult to distinguish between them. The bean starches are the largest, and the lentil the smallest, but these differences in size are insufficient for differentiation. The bean is more flattened than the pea, and has more often a puckered hilum.

The ovoid starches have all well-marked concentric striæ, with circular or short slit hila. In potato the hilum tends to appear at the small end, which, with the striæ and shape, gives an appearance not unlike an oyster, while in arrowroot the hilum is generally at the larger end. With the exception of the variety known as 'Tous le Mois,' the various arrowroots used in this country (Bermuda, St. Vincent, and Natal) are smaller than the potato granules.

Sago and tapioca starches very often present a semi-faceted shape, suggestive of a bell or a guardsman's busby. They are easily differentiated by the relative sizes, the sago granule being much larger than that of tapioca.

The three faceted starches are maize, oat, and rice. The maize granules are by far the largest in size of

the three, and generally exhibit a well-marked stellate hilum. The oat granules are slightly larger than those of rice, and are frequently to be seen united in a spherical formation, while the rice granules display an angular formation.

The starches of wheat, maize, and rice are official in the British Pharmacopœia, 1914. We give below the average percentage composition of some of the common farinaceous materials.

	Water.	*Proteins.*	*Fats.*	*Carbo-hydrates.*	*Ash.*
Arrowroot ..	15·40	0·80	—	83·5	0·30
Barley meal ..	11·30	12·70	2·00	71·00	3·00
Flour	13·50	13·00	1·50	71·30	0·70
Maize	13·50	10·00	6·70	64·50	1·40
Oatmeal	15·00	13·00	6·00	63·00	3·00
Peas	15·60	22·60	2·00	58·00	2·40
Rice	10·00	5·00	0·10	84·40	0·50
Rye meal ..	14·00	11·00	2·00	71·25	1·75
Bean	11·50	26·25	2·50	57·50	2·25
Potato flour ..	74·00	2·00	0·15	22·85	1·00
Sago	14·00	0·8	—	85·05	0·15
Tapioca	13·40	0·55	—	85·95	0·10

(The last five analyses are by Kenwood.)

RICE.

A grain of rice from which husk and cuticle have been removed in the processes of hulling and milling is dull in appearance. The grain is often 'faced' or polished by the application of talc, French chalk, or steatite, mixed with glucose or oil. Oil tends to impart translucency to the grain. To increase the whiteness, ultramarine, Prussian blue, indigo, or coal-tar dyes are often used.

The total ash of milled but unpolished rice varies from 0·2 to 0·9 per cent., though few samples exceed 0·6 per cent. The ash of such rice, insoluble in hydrochloric acid, varies from a trace to 0·06 per

cent. These data may show the presence or absence of added mineral matter, but the evidence afforded may be inconclusive or, at best, approximate. However, C. H. Cribb and P. A. E. Richards have noticed (*Analyst*, 1906, p. 40) that the ash of genuine rice has a glassy texture, while that of rice polished with talc is flaky.

The talc may be estimated by Krźiźan's process (*Analyst*, 1906, p. 263): 20 grammes of the sample in a beaker are covered with hydrogen peroxide (10-volume strength is ample). A little dilute ammonia solution is added, and the beaker warmed to 60° C. or 70° C. for, say, ten minutes. The bubbles of gas that form between the grain and its coating detach the particles of talc. The turbid liquid is decanted, the grains washed three or four times with distilled water, and the washings added to the first liquor. This liquid contains some meal in suspension. It is rendered acid with hydrochloric acid, chromic acid (or potassium chlorate) is added, and the liquid boiled. The meal having thus been oxidised, the talc is filtered off, washed with water, and ignited at the lowest possible temperature. From unpolished rice, Krźiźan's process produces only a small amount of mineral residue, which, in our experience, ranges from 0·005 to 0·025 per cent.

Krźizan found that in ashing rice a distinct proportion of the talc, by fusion with the normal mineral matter of rice, is rendered soluble in acid. A calculation of the proportion of talc, based on the mineral matter insoluble in hydrochloric acid, usually, therefore, gives too low a result.

E. W. T. Jones (*Jour. Soc. Chem. Ind.*, 1915, March 15) heats the rice with ether, which is then decanted; then with water, which is also decanted. The whole of the talc comes away in these two extracts, together with any oil used. The figures for mineral matter agree with those obtained by Krźiźan's process, our own experience with Jones's process, which is limited, being that it gives figures slightly below those got by the other process.

Hamill (*Reports of Inspectors of Foods*, 1909, No. 8) says 'an outside limit of not more than 0·5 per cent.

of mineral matter would seem amply to meet the requirements of traders who represent this practice as necessary'—an opinion from which many differ. To support the practice, millers have claimed that polished rice is less liable to attack by weevils. This does not appear to be supported by any trustworthy evidence. The objections to the practice are many. Cribb and Richards (*loc. cit.*) suggested the production of mechanical irritation in the body by the particles and the formation of fæcal concretions. In point of fact, a pancreatic calculus having the composition of French chalk has been described (W. F. Lowe and J. G. Taylor, *Lancet*, June 18, 1910).

The deeper layers of the pericarp (the *silver skin* of Dutch writers) contain some substances essential to the maintenance of health (vitamine) in those whose staple diet is rice. This is removed on polishing. The natives of Oriental countries who consume unpolished rice do not suffer from beri-beri, as do those who take polished rice. Fowls fed on polished rice develop a form of polyneuritis analogous to beri-beri. If the polishings removed from the rice are added to polished rice, fowls fed on the mixture keep healthy.

PEARL BARLEY.

The total ash of genuine pearl barley ranges from 0·70 per cent. to 1·1 per cent., and the ash soluble in dilute hydrochloric acid from a trace to 0·09 per cent.

Pearl barley is sometimes faced with talc, for the estimation of which the processes given for rice are available. Rice powder is frequently used for facing barley. J. F. Liverseege and H. Hawley (*Jour. Soc. Chem. Ind.*, 1915, p. 203) shake some of the sample on a No. 20 sieve. Samples faced with talc usually yield no dust, but those faced with rice give a dust. Ten grammes of the sieved barley are then rapidly washed in a small glass dish with five separate quantities of 10 c.c. of water. An aliquot part of

the washings is evaporated to dryness and weighed. The remainder of the washings is centrifuged, and the amount of solids in solution having been determined, a correction for this is deducted from the amount of dry solids removed by washing with water. Microscopical examinations of both dust and washings are made to determine the proportion of rice starch in them. These authors found twenty-two out of twenty-three samples that were unfaced with rice or mineral matter to yield less than 0·5 per cent. of dust, the remaining sample yielding 1·27 per cent.

In pearl barley the attrition is carried farther than it is in 'pot barley,' where only the outer cuticle is ground off. Hence both total and insoluble ash are likely to be higher in the latter. McGill (*Canadian Bulletin*, No. 329), reporting on 108 samples of pot barley, found the total ash to vary from 0·90 to 1·46 per cent. and the insoluble ash to vary from 0·04 to 0·11 per cent.; except in one district, where both tended to higher figures and the article ('Orge Mondé') when unfaced gave total ash up to 2·29 per cent. and insoluble ash up to 0·14 per cent.

SAGO.

Sometimes, when sago is asked for, a variety of tapioca known as 'pearl tapioca' is supplied, which, although the same shape and size as sago, is white instead of muddy yellow, and is free from the slightly earthy taste of sago. It consequently gives the purchaser the idea that it is purer. Such substitution has been held to be not to the prejudice of the purchaser (Sandys *v.* Rhodes, 1903).

The Local Government Board (1909-10) say 'these articles are of nearly equal value, and the offence is therefore slight, but there seems no reason why they should not be sold under their proper names.'

OATMEAL.

Of recent years a number of prepared oat products have to a large extent supplanted the old-fashioned oatmeal as a breakfast food. Harcourt (*Jour. Soc. Chem. Ind.*, 1907, p. 240) gives an account of the composition, digestibility, and cost of such foods. There is apparently some question as to these foods being more digestible than the old granulated oatmeals, and there appears no evidence to support the extravagant claims made for some of them. Macfarlane (*Canadian Bulletin*, No. 127) found that the crude fibre in 155 samples of rolled oats and oatmeal varied from 0·80 to 3·35 per cent., and suggests that 2 per cent. of crude fibre should be regarded as the highest allowable limit. He found the average proteins to be 12·30 per cent., and the average fat 4·67 per cent., which show less nutrient value than the percentages of 13·87 of proteins and 6·18 of fat obtained by König on oatmeal.

WHEAT-FLOUR.

Flour is the meal produced by grinding and bolting wheat; the various coats of the grain are thus more or less removed as bran. When the separation of bran is less complete, the flour is known as 'wholemeal flour.' Some difference of opinion exists as to what coverings or parts of the grain should be removed to give the consumer the best value. The Bread and Food Reform League demand (*Miller*, January 4, 1915) the following meals and flours, unbleached and made from well-cleaned, properly selected wheats, free from 'improvers' or inorganic mineral substances.

Wholemeal.—The whole grain thoroughly and evenly ground and re-ground, so fine that every particle will pass through a 16 or 18-mesh sieve. No particle should be larger than a pin's head.

Wheatmeal.—Six to ten per cent. of the coarse bran is removed, and the remainder of the wheat grain

ground so fine that no particle is larger than a pin's head.

Old-Fashioned Household Flour (*'Standard'*).—This flour should have at least 80 per cent. of the whole wheat, including the germ and all the semolina, none whatever being extracted for 'Patents.'

'Straight Run' Household Flour.—This flour should be a straight-run flour including the germ, and should contain not less than 72 per cent. of the grain.

Retention of the germ is advocated on various grounds: It is richer in phosphorus-containing compounds (*e.g.*, nuclein) than the rest of the grain, and contains certain amino groupings essential for growth and readily available for nutrition. In it are supposed to be accessory substances necessary for growth and support of life. Various arguments are adduced for the exclusion of the germ from household flour. It is said that the oil of the germ is readily oxidised, with the quick development of unpleasant taste and smell. The germ contains bodies which do not permit the baker to conduct the process of doughing so as to allow proper peptonisation of the proteins. Flour containing germ will not keep. The deterioration commences from the time of manufacture. Millstones do not readily reduce germ to flour, consequently a large proportion is removed in the operation of dressing or bolting, passing away with the offals, and not into the finished flour.

While wholemeal bread is richer in protein than white bread the difference is not large. Wholemeal bread is not so readily digested by most people as white bread is, so that any increase in protein percentage is more than counterbalanced by increased loss in the fæces. Newman, Robinson, Halnan and Neville (*Journal of Hygiene*, 1912, p. 119), feeding men on white and 'standard' bread found that the phosphorus compounds which are more abundant in bread of the standard type are no worse absorbed than those in white bread. In breads containing more of the whole wheat berry than 'standard' bread, the availability of both nitrogen and phosphorus proved to be decidedly less. Further in-

formation may be got from Dr. Hamill's 'Report to the Local Government Board on the Nutritive Value of Bread made from Different Varieties of Wheat-Flour,' Food Reports, No. 14, 1911.

When the Sale of Food and Drugs Act, 1875, was passed, 'household flour' certainly contained the 'patents' and 'germ.' It has therefore been suggested that their removal is an offence under Section 9 of that Act. No decision appears to have been sought on the point.

Moisture.—Flour should not contain more than 13 or 15 per cent. of moisture; more than this impairs its keeping properties, and favours the growth of bacteria, moulds, and parasites.

Gluten.—Flour contains five proteins, three of which are only present in traces, and the other two —gliadin and glutenin—form a stringy mass with water, known as 'gluten.' Flour contains from 8 to 12 per cent. of gluten, which is estimated by mixing 25 grammes of flour in a coffee-cup with 15 c.c. of water (temperature not to exceed 15° C.) and working the mass into a ball with a spatula. After standing for an hour, the dough is kneaded in a stream of cold water until starch and soluble matters are removed. The gluten left is placed in cold water for an hour, then pressed as dry as possible between the hands, rolled into a ball and weighed as moist gluten. The gluten is then spread over a dish, dried for twenty-four hours in a boiling water-oven, and dry gluten weighed. (Method of the U.S. Department of Agriculture.)

Jago's doughing test is performed thus: 50 grammes of the sample are 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 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.

Mineral Additions (with the exception of alum, which is used in too small a quantity to affect the figure) would be shown by an increase in the ash, and should this be above 0·7 per cent., the following procedure should be adopted for the separation: 100 grammes of the flour are shaken in a separator with 200 c.c. of chloroform. After allowing to stand till the flour has risen to the top, the mineral matter which has sunk can be drawn off from the bottom, dried, weighed, and examined microscopically. Any soluble matter may be dissolved out and examined for alum, while the insoluble matter is again dried and weighed; and if it should be more than 0·1 per cent., it should be further examined for calcium sulphate, barium sulphate, and chalk.

Alum is detected by the process given in the chapter on 'Bread.'

'Improvers.'—Various substances are sold to millers under this euphonious, but misleading, name with the intent to increase the strength of wheat. In plain English, they permit flour to take up more moisture and consequently the sale of a wetter bread. By their use, a weak wheat—that is, one deficient in gluten—may be made to serve as well as a strong, or rich in gluten, wheat, the result being that the consumer gets more water and less protein in his bread. Phosphatic compounds are popular (acid potassium phosphate, acid magnesium phosphate, and bi- and tri-calcium phosphates), as they stimulate the action of yeast in bread-making in addition. They can be detected by Curtel's method (abst. *Analyst*, 1910, p. 398): 5 grammes of the sample are shaken with 50 c.c. of carbon tetrachloride, the mixture centrifuged, and the sediment dissolved in nitric acid and tested for phosphates. Pure flour yields no phosphate reaction.

Potassium persulphate has been used as an improver and is detected by a method proposed by E. Hinks (*Analyst*, 1912, p. 90). A 2 per cent. alcoholic solution of benzidin is poured over the dry flour, when an inky blue colour develops round each particle of persulphate. In the dry flour the persulphate is stable. We find that a sample over five years old still reacts to the test.

Monnier has proposed the use of methylene blue as a test for persulphates, with which it forms a red compound. We have applied this to flour containing persulphates, getting various shades of lavender and lilac, while pure flour does not alter the blue of the dye. But the test is decidedly less striking than that with benzidin.

Self-Raising Flour.—This article is sold containing the necessary constituents for the production of gas. These are generally sodium bicarbonate and some 'cream of tartar substitute.' For the latter, acid sodium phosphate has been recently introduced, but it is said that the soluble sodium salts leave a bad taste in the bread, and as a rule acid calcium phosphate is used as the acid constituent. The total ash on self-raising flour (G.R. flour) ranges from 2 to 3 per cent. (plain G.R. flour varies from 0·5 to 0·9 per cent.). Acid calcium phosphate is very liable to contain arsenic, and as found in commerce invariably contains calcium sulphate. Hamill (L.G.B. Food Reports, No. 13) recommends that acid calcium phosphate used in the preparation of food should not contain more than 10 per cent. of calcium sulphate.

Sulphates occur naturally in flour, but any determinations made on the ash are certain to be below the truth. In the first place, much of the SO_3 is in organic combination, principally with proteins, while even if present as added calcium sulphate much is lost during ignition. Cripps and Wright (*Analyst*, 1914, p. 429) have shown loss of SO_3 to occur when mineral sulphates are ignited with phosphates. They found pure flour to contain from 6·9 to 10·3 parts of SO_3 per 100,000. R. T. Thomson (*Analyst*, 1914, p. 527) considers that a fair allowance for SO_3 naturally present in a flour would be one-fortieth of the mineral matter, if no other mineral matter has been introduced. The process for estimating sulphates given for baking-powder is applicable to those in flour, whether natural or due to persulphates or to calcium sulphate.

Bleaching.—Flour is extensively bleached by the halogens, and by ozone and oxides of nitrogen developed by electrical discharges. This has the

effect of making an inferior article resemble a superior one.

Flour that has never been bleached contains a little nitrite, or at any rate a nitrite-reacting substance. Hamill (L.G.B. Food Reports, No. 12) found as much as 0·5 part per million of nitrites (expressed as $NaNO_2$), and says: 'For practical purposes, however, it may be presumed with some probability that when more than one part of nitrites per million is present the flour has been bleached; with quantities much above this the inference of bleaching amounts to practical certainty.'

Later, Monier-Williams (L.G.B. Food Reports, No. 19) advised caution in the interpretation of the results of the Griess-Ilosvay test, but thought it extremely improbable that unbleached flour, stored under ordinary conditions, will show more than 1·5 to 2·0 parts of sodium nitrite per million by this test. The nitrite-reacting substance in unbleached flour tends to increase on storage, hence the latitude necessary in interpreting results.

Rockwood (*Jour. Biol. Chem.*, 1910, p. 327) found the artificial digestion of unbleached flour, as compared with specimens of the same flour bleached with nitrogen peroxide, to show no loss of digestibility. E. F. Ladd (*British Food Journal*, November, 1909) found injury results to the gluten, a finding confirmed by Harden. Monier-Williams found bleaching to exercise an inhibitory effect on the salivary digestion of flour.

It appears that, without further legislation, the bleaching of flour by nitrogen peroxide cannot be dealt with under the Sale of Food and Drugs Acts.

Griess-Ilosvay Test.—A standard solution of sodium nitrite, best prepared from silver nitrite and sodium chloride, containing 0·000005 gramme of sodium nitrite per c.c., is required. The reagent consists of two solutions: (*a*) sulphanilic acid, 0·5 gramme; glacial acetic acid, 30 c.c.; water, 120 c.c. (*b*) 0·2 gramme alpha-naphthylamine chloride is dissolved in 20 c.c. strong acetic acid with the aid of heat. The clear solution is poured off and made up to 150 c.c. with 20 per cent. acetic acid.

Twenty-five grammes of the flour are shaken up with 250 c.c. of water for fifteen minutes. Tap-water is usually free from nitrite and can be employed. If distilled water is used, it must be free from nitrite. The flour suspension is filtered and 50 c.c. of the filtrate tested with 2 c.c. of (*a*) and 2 c.c. of (*b*). The pink tint, accentuated by warming to 80° C. for ten minutes, is compared with suitable quantities of the standard in similar bulk of nitrite-free water. Filter-paper sometimes contains nitrite, and this source of error must be excluded.

Phosphoric Acid is estimated by W. F. K. Stock's modification of the molybdate of ammonia process. The ash of the sample is treated with nitric acid, the solution diluted and filtered. About 20 c.c. of strong ammonia is 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 c.c. 2·5 c.c. of fuming nitric acid is added, and the solution is warmed to 70° C., and 20 c.c. 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 c.c. 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 0·0373, which will give the amount of phosphorus as P_2O_5.

In many foods, especially in meat, meat-juices, eggs, and milk products, much of phosphorus is in the form of phosphatides. Some loss of phosphorus in this form may be expected during simple ignition, and Vozárik has proposed the following method of ashing: 1 to 3 grammes of the finely ground substance are carefully mixed with 0·2 gramme of magnesia in a platinum crucible, and carbonised, the

crucible being supported obliquely with the lid off. When the flame goes out the lid is replaced, and the crucible strongly heated until the contents are completely ashed. The phosphoric acid is then estimated in the usual manner.

Two foreign seeds possessing toxic properties are sometimes found in flour—the corn-cockle (*Agrostemma githago*) and darnel seeds (*Lolium temulentum*). The former is detected by its appearance as large black seeds, and the latter by the repulsive taste and the greenish colour produced on the addition of alcohol. Acetic and lactic fermentations also occur in unsound flour. The corn-weevil (*Calandra granara*) can be seen with the naked eye, but the wheat-mite (*Acarus* or *Tyroglyphus farinæ*) and the 'red blight,' 'eel blight,' or 'ear-cockle' (*Vibrio tritici*), require microscopical examination for their detection. The principal vegetable parasites of wheat are bunt (*Uredo fœtida*) and *Tilletia caries*, which are similar in microscopical appearance, looking something like peppercorns; 'smut' (*Uredo* or *Ustilago segetum*), oval brown spores; and 'mildew,' or 'red rust' (*Puccinia graminis*), the ripe sporangia of which appear microscopically as dark brown club-shaped bodies. 'Smut' is more common in rye, oats, and barley than in wheat, and bread made from flour containing it has a bluish colour. *Mucor*, *Aspergillus*, and *Penicillium* should be looked for in mouldy and decomposing flour and bread.

Rye is sometimes affected with ergot (*Oïdium abortefaciens*). When the flour so affected is treated with potassium hydrate solution, an odour of trimethylamine is noticed. Maize may be affected with *Ustilago maydis*.

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 carbon dioxide.

2. By the use of baking-powder 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's 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. Potato starch may, however, be detected by the readiness with which it stains by thionine blue, methylene blue, neutral red, or 'metachrome-red G Agfa.'

Many bakers add a small quantity of boiled potatoes (about 1 per cent.) to their dough. This renders the bread white, and is not the outcome of fraudulent intent.

In sampling bread for analysis, 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.

Alum increases the whiteness and apparent quality of inferior flour. The logwood test will detect 7 grains of alum in a 4-pound loaf.

Logwood Test.—A freshly prepared alcoholic tincture of logwood (made by digesting 5 grammes of fresh chips or raspings in 100 c.c. alcohol), and a saturated solution of ammonium carbonate, are required.

Flour is tested as follows: 10 grammes of the sample are made into a paste with 10 c.c. of distilled water; 1 c.c. each of the logwood tincture and the ammonium carbonate solution are then added, and the whole well mixed with a glass rod. If the sample is free from alum, the mixture is of a pinkish colour, gradually fading to a dirty brown; but in the presence of alum the pink colour is changed to a lavender tint or actual blue colour. The sample should be put into the water-oven for two hours to make certain that the colour is permanent.

Bread is tested as follows: 5 c.c. each of the logwood tincture and ammonium carbonate solution are mixed and made up to 100 c.c. with water; this is poured without delay over a lump of bread free from crust weighing about 10 grammes. After about five minutes, when the bread has soaked up the liquid evenly, the excess of fluid is drained off, and the bread dried in the dish at 100° C. If alum is present, the sample assumes a light violet or blue tint, which becomes more marked on drying. With bread free from alum the purplish tint first obtained fades to a buff or light brown colour.

Sour bread and some other mineral substances besides alum may give the logwood reaction, and therefore the results must be accepted with caution. If alum is indicated by the logwood test, estimations of alumina and sulphates will be necessary.

Copper Sulphate has been detected in bread, its presence being probably due to the corn having been steeped in a copper solution before sowing to avoid fungoid growth. It is detected by soaking the bread in a very weak solution of potassium ferrocyanide acidulated with acetic acid. A purplish or reddish-brown coloration indicates the presence of copper.

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

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

The water should not exceed 40 per cent., but brown breads contain more water than ordinary bread, and more latitude should be allowed them.

The **Ash** of flours and meals is difficult 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 solution, then dry and carefully ignite. After about two treatments of this kind, a clean ash is readily obtained. The dish in which the

ash is being obtained may with advantage be covered with a strip of platinum.

The total ash should not exceed 2 per cent., and the ash insoluble in hydrochloric acid should not exceed 0·2 per cent. The ash of bread is greater than that of the flour, owing to the addition of common salt and baking-powder.

Determination of Silica and of Added Alum.—One hundred grammes of the bread or flour are carefully incinerated at a moderate heat so as not to fuse the ash. The process is completed by adding pure sodium carbonate and a little nitre, and heating the mixture to fusion. The fused mass is dissolved in water and rinsed into a beaker, carefully acidulated with hydrochloric acid, evaporated to dryness, and again taken up in acid; the residual silica is washed, dried, ignited, and weighed as SiO_2. To the total filtrate dilute ammonia is added until the precipitate barely redissolves on stirring, when a slightly acid solution of ammonium acetate is added and the solution brought to the boil, and then allowed to stand some hours. The precipitate of aluminium and iron phosphates is filtered off, washed, and redissolved in the smallest possible amount of hydrochloric acid. The resulting solution is poured into an excess of an aqueous solution of pure caustic soda free from alumina, contained in a platinum dish. After heating for a short time the solution is considerably diluted and filtered. The filtrate is acidulated with hydrochloric acid, ammonium acetate, and a little of a solution of sodium phosphate added, and then a slight excess of ammonia. The solution is warmed until all smell of ammonia is lost, when it is filtered, and the precipitated aluminium phosphate is washed, ignited, and weighed. The amount of aluminium phosphate obtained multiplied by 3·713 will give the ammonia alum (crystallised), or by 3·883 the amount of potash alum (crystallised), in the 100 grammes of sample taken. In making this estimation, porcelain vessels must be avoided, and alkaline liquids must not be heated in glass.

While properly cleaned wheat is said to contain no trace of alumina, particles of clay are apt to get

into flour, and Blyth says there is no second-class flour in commerce which does not contain some small percentage of alumina. Carter Bell and Dupré demonstrated the existence of a rough ratio between alumina and silica in flour and bread to which no alum has been added. Blyth selected a ratio of 1 part of alumina to 7·1 parts of silica as a fair statement. If the figure for alumina be converted into terms of crystallised ammonia alum, it is seen that the amount of silica is practically equal to that of ammonia alum. Hence, it is usual to allow for every part of silica found 1 part of alum, and this quantity is deducted as natural to the flour in the final calculation. The percentage of alum multiplied by 280 gives the number of grains per 4-pound loaf. The number of milligrammes of $AlPO_4$ per 100 grammes of bread gives without calculation a close approximation to the number of grains of ammonia alum per 4-pound loaf (A. H. Allen).

BAKING-POWDER.

Baking-powder may be defined as 'a salt or mixture of salts, with or without a diluent such as starch, which evolves carbon dioxide when moistened and on heating' (Moor).

Before the Sale of Food and Drugs Act of 1899 baking-powder was recognised neither as a food nor a drug, and no action could be taken if it contained alum or other noxious substance, although a baker who used such baking-powder could be convicted because the bread was a food. The Act referred to defined 'food' as including 'every article used for food or drink by man, other than drugs or water, and any article which ordinarily enters into or is used in the composition or preparation of human food, and shall also include flavouring matters and condiments.' As a consequence prosecutions for the presence of alum in baking-powder became frequent and successful, as the pharmacological evidence is strongly against its use in food. If the alum be in

excess, it inhibits action of the digestive ferments; the resulting sulphate of soda has a purgative action, and the alumina set free during the reaction is capable of rendering insoluble and unavailable the phosphoric acid and phosphates present in the food. Similarly bisulphate of potash is objectionable on account of the purgative character of the resulting salt.

The carbonate used in baking-powders is bicarbonate of soda, and the acid constituent may be cream of tartar or acid phosphate of lime. All have fillings composed of milk-sugar or starch (generally rice).

Ruttan says that 'bread made with tartrate powders is most quickly digested, because the Rochelle salts formed possess a very weak retarding action on ferments.' The value of the cream of tartar is enhanced by the slowness with which it reacts with the bicarbonate of soda. The cream of tartar powders keep well, and, as they react in a perfectly definite way, it is easy for a manufacturer to guarantee that neither component shall be in excess.

Carbonate of ammonium is unobjectionable as a constituent of baking-powder; so also is superphosphate of calcium if free from calcium sulphate, and practically free from neutral calcium phosphate. This article is usually sold as a 'cream of tartar substitute.' It is never found in commerce free from sand, for which 0·5 per cent. is probably a reasonable maximum It has already been dealt with under 'Self-Raising Flour.'

The ideal baking-powder giving the maximum gas-producing power is indicated by the following formula:

$$\underset{188}{KHC_4H_4O_6} + \underset{84}{NaHCO_3} = \underset{210}{KNaC_4H_4O_6} + \underset{18}{H_2O} + \underset{44}{CO_2}.$$

That is to say, 1 gramme of a powder in the above proportions would yield approximately 81 c.c. of gas, at N.T.P., equivalent to 16 per cent. by weight of CO_2. This would be reduced by the presence of filling; about 20 per cent. is a fair amount.

Baking-powders partly dependent on the effect of heat alone on sodium bicarbonate come in a different category, as do those containing acid calcium phosphate.

The Analysis of Baking-Powder. — Microscopical examination of the residue insoluble in cold water will determine the nature of the filling.

The following determinations are usually required. A determination of the alkalinity or acidity, as the case may be, of the aqueous solution of the powder is useful as showing if any great excess of acid or alkaline constituents is present.

Available Carbon Dioxide.—This estimation cannot be used with phosphate or simple bicarbonate powders. It is made by acting upon the powder with water, and measuring the resulting gas given off. The best form of apparatus for exact determinations is that recommended by Fresenius, in which the gas is absorbed with soda-lime, or one of the forms of the Schrötter type may be used, although they are apt to give results below the truth if not carefully used. Excellent comparative results may also be obtained in the apparatus used in determining urea in urine (see also Macara, *Analyst*, 1915, p. 272).

Estimation of Tartaric Acid.—Five grammes of the sample are weighed out and washed into a 500 c.c. flask with about 100 c.c. of water; 15 c.c. of concentrated hydrochloric acid is added, and the whole diluted with water up to the mark. The starch and other insoluble matter are allowed to settle, and the supernatant liquid filtered. To 50 c.c. of the filtrate (=0·5 gramme original) is added 10 c.c. of a 30 per cent. solution of carbonate of potash, and the solution boiled for half an hour; it is then filtered into a dish, and the filtrate and washings evaporated to a bulk of about 10 c.c. Add gradually with constant stirring 4 c.c. glacial acetic acid, and then 100 c.c. of 95 per cent. alcohol, stirring the liquid until the precipitate assumes a crystalline appearance. After the liquid has stood long enough for this precipitate to form and settle, best for several hours, decant through a small filter, add alcohol to the precipitate, and bring it on to the filter, wash out the dish, and

finally the filter, with alcohol until it is entirely free from acetic acid. Transfer precipitate and filter to a beaker, add water, and boil, washing out the dish with boiling water, if any precipitate adheres to it. The resulting liquid is titrated with decinormal alkali, using phenolphthalein as indicator. Each c.c. of decinormal alkali = 0·0188 gramme of potassium bitartrate, or 0·0150 gramme of tartaric acid. Tartrates can be estimated by the polariscope (Richardson, *Jour. Soc. Chem. Ind.*, 1903, p. 405).

Phosphoric Acid.—Estimated by Stock's method (p. 103).

Estimation of Alum (Leach's Method).—Two grammes of the sample are ashed in a platinum dish. The ash is extracted with boiling water and filtered. To the filtrate is added sufficient ammonium chloride solution to produce a distinct odour of ammonia. A flocculent precipitate indicates the presence of aluminium. Filter off precipitate, dissolve in nitric acid, and test for phosphates with ammonium molybdate solution. If present, these must be determined separately. The process given above is repeated. After igniting the residue obtained and weighing, the P_2O_5 (if present) is subtracted from the weight. The difference will be the Al_2O_3. Phosphates do not interfere with the process, since calcium phosphate is left insoluble, while soluble phosphates cause the aluminium to be precipitated as $AlPO_4$.

Estimation of Sulphates.—0·5 to 1 gramme of the sample is boiled with very dilute hydrochloric acid until all the powder, including the starch, goes into solution; filter; barium chloride is added in slight excess to the filtrate, and the solution allowed to stand some hours. The barium sulphate is then filtered off, washed, dried, ignited, and weighed.

In Victoria a baking-powder must not contain more than 1 per cent. of potassium sulphate or calcium sulphate, alum must be absent, and the yield of carbon dioxide must be not less than 8 per cent. by weight.*

* The same requirements were proposed in 'Suggested Standards' (1902).

'Egg Substitute' Powders. — These are merely baking-powder coloured to a yellow tint. Turmeric is usually found, but lead chromate in the proportion of approximately 0·5 per cent. has been used in ignorance.

VINEGAR.

Vinegar has been defined as 'the product of the alcoholic and acetous fermentations of a vegetable juice or infusion.' This definition includes all kinds of brewed vinegar, but excludes wood-vinegar.

Malt-vinegar could formerly be defined as 'vinegar brewed either from malted barley or from a mixture of malt and barley.' Such an article yields characteristic figures on analysis, which distinguish it from glucose vinegar or vinegar brewed from substances other than malt. It varies 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, the other constituents should vary in proportion with the acetic acid.

The use of other material for malt-vinegar is now permitted. The Local Government Board (*Rept. Med. Off.*, 1911-12) define malt-vinegar as derived wholly from malted barley or wholly from cereals, the starch of which has been saccharified by the diastase of malt.

The present tendency of vinegar brewers is to aim at a distiller's mash (*i.e.*, complete alcoholic fermentation) and to use a good deal of rice or maize in the mash tun. The consequence is that so-called 'malt-vinegar' may, compared with the analysis given above, be low in specific gravity, in total solids, in ash, in phosphoric acid, and in nitrogen, and yet be entitled to the name. On these criteria alone it

becomes a difficult matter to distinguish the presence of even large proportions of 'vinegar other than malt.'

A clue to the origin of the vinegar may often be obtained. A vinegar derived principally from grain which has been converted by acid hydrolysis will probably have a relatively high ash rich in sulphates and low in its alkalinity. A vinegar brewed chiefly from glucose and molasses will have a low ash, while the presence of up to, say, 20 per cent. of unfermentable matter in commercial glucose may result in a vinegar of high gravity. A high gravity will also result if much fermentable, but unfermented, material is present, though this is counter to good and economical brewing, which aims at the preparation of a well-attenuated wash.

If no clarifying agent such as potassium ferrocyanide has been used, the proportion of nitrogen is useful in diagnosis of origin. Compared with the phosphoric acid, the nitrogen figure may be high where rice has been used, and will also be high where green malt has been employed if the rootlets have been added to the mash tun.

Commercial acetic acid contains traces of formic acid, and gives a means for identifying the former in vinegar. Rowat (*Canadian Bulletin*, No. 364) finds that malt-vinegars give no distillate which could be mistaken to contain formic acid, and that the depth of colour that traces of formic acid give with fuchsin in Woodman and Burwell's process is approximately proportional to the amount of acetic acid added.

Vinegar prepared from malted maize gives a high figure for total solids, and low figures for nitrogen and phosphoric acid, compared with those for a malt (barley) vinegar. The following analysis by J. S. Jamieson (*Analyst*, 1915, p. 106) is on a vinegar prepared from germinated maize and pasteurised:

Specific gravity	1·019
Total solids	3·66 per cent.
Ash	0·36 ,,
Nitrogen	0·009 ,,
Phosphoric acid	0·02 ,,
Acetic acid	4·20 ,,

In vinegar-making the malt or malt and barley (the latter finely ground) are 'mashed,' and soaked in successive quantities of hot water till all that is soluble is extracted. The clear liquor is cooled and run off into another vessel, and yeast added. Alcoholic fermentation takes place, with evolution of carbon dioxide. The 'wash' is then pumped over piles of birch-twigs or wicker-work placed in high vats, to which a regulated supply of air is allowed. The twigs become coated with *Mycoderma aceti*, 'vinegar plant,' which converts the alcohol 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, the little left improving the flavour and assisting the 'keeping' of the finished product, which is generally kept for a year in order that the flavour may fully develop.

The Local Government Board (*loc. cit.*) define vinegar as a liquid derived wholly from alcoholic and acetous fermentations, containing not less than 4 grammes acetic acid per 100 cubic centimetres, and not more than 0·0143 milligramme of arsenic in the same quantity. It must contain no other acids, no lead or copper, and no foreign substances or colouring matter except caramel. Artificial vinegar is defined as any vinegar or substitute for vinegar containing, or derived from any preparation containing, any added acetic acid not wholly the product of alcoholic and acetous fermentations. It must comply with the other requirements mentioned in relation to vinegar.

Malt-vinegar is required to be dextro-rotatory by the United States Department of Agriculture. A. C. Chapman criticises this and shows how malt-vinegar may sometimes be lævo-rotatory owing to the presence of proteins or the products of their hydrolysis (*Analyst*, 1912, p. 123).

'Distilled' or 'white' vinegar, largely used in the North of England, is usually prepared by distilling malt-vinegar.

'Wood-vinegar,' so called, is prepared by diluting acetic acid. This is sometimes coloured with caramel, and sold as malt-vinegar. It 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.

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.

The best wine-vinegar is made from white wine in France, and contains from 5 to 5·6 per cent. of acetic acid (Hamill). The total solids should be not less than 1 per cent. and the ash not less than 0·25 per cent. Allen says that genuine wine-vinegar always contains acid potassium tartrate. Dilute acetic acid is sometimes sold as 'white-wine vinegar,' or 'Orleans vinegar.'

Vinegar is liable to metallic contamination from the apparatus used in its manufacture, copper having been found on several occasions. Arsenic may also be present, derived from arsenical malt, caramel, or glucose.

Potassium ferrocyanide is sometimes used in clarifying vinegars, and this has been shown by Harden to be acted on by acetic acid with the production of ferrocyanic acid, which oxidises into Prussian blue and hydrocyanic acid. The prussic acid appears to form an unstable combination with the organic constituents of the vinegar, and, although there is no proof of its toxicity in this combination, Hamill thinks there is sufficient ground for doubt in the matter to cause the process to be regarded with considerable suspicion.

To improve its keeping qualities, vinegar is sometimes submitted to pasteurisation at about 145° F. To attain the same end, calcium bisulphite, boron compounds, formaldehyde, and sulphuric acid are also sometimes used. At one time vinegar was an excisable article, and for its preservation sulphuric acid was allowed to be employed 'in the proportion not exceeding one-thousandth part thereof by weight.' The duty on vinegar was removed in 1844,

and the addition of sulphuric acid would now constitute an offence. The practice has apparently died out.

Analysis of Vinegar—Specific Gravity.—In the case of a strong vinegar—*i.e.*, 5 per cent. acetic acid—this should be about 1·019. The London and County Vinegar Brewers' Association suggested 1·017 to 1·021 as the range of gravity for such a vinegar. The specific gravity of an artificial vinegar will naturally depend upon the content of acetic acid, malt-vinegar, and caramel.

Acetic Acid.—Ten c.c. should be titrated with $\frac{N}{2}$ soda, using phenolphthalein as indicator, after well diluting with distilled water, a beaker containing the same amount of vinegar diluted in the same way being used as a foil, when:

No. of c.c. of $\frac{N}{2}$ NaHO × ·03 × 10 = per cent. acetic acid.

The **Total Solids** are determined by evaporating 25 c.c. in a tared platinum dish; this, after drying to constant weight, is ignited at a low temperature to obtain the ash. A proportion of the acetic acid remains in the total solids. It can be removed by three evaporations (Russell and Hodgson).

Nitrogen is determined by Kjeldahl's process (see under 'Milk') on 25 c.c. of the sample. If a clarifying agent such as potassium ferrocyanide has been used, a lower nitrogen figure will be obtained.

Phosphoric Acid can be estimated by Stock's method (see under 'Self-Raising Flour').

Free Sulphuric Acid can be detected by metanil yellow (*Analyst*, 1908, p. 329). It may be estimated by a method 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.

Fifty c.c. of the sample is evaporated to dryness in a platinum dish with 25 c.c. $\frac{N}{10}$ NaHO, and then ignited at the lowest possible temperature. Twenty-five c.c. $\frac{N}{10}$ HCl is 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

phenolphthalein. The number of cubic centimetres of soda used is multiplied by 0·0049, which gives the amount of free sulphuric acid in 50 c.c. of the sample.

Vinegar from hydrolysed grain contains a relatively large amount of sulphates, and vinegars have been reported as containing added sulphuric acid, when waters containing large amounts of sulphates had been used in the manufacture. It is therefore necessary to ascertain that there is more sulphuric acid present than the mineral bases could have combined with. Sulphates must be estimated directly on the sample, as loss of SO_3 occurs on ashing.

TEA.

Tea is the prepared leaf of the *Thea sinensis*, *Thea assamica*, and allied species belonging to the genus *Camellia*. Black and green teas are the product of the same plant, the difference in colour being due to the mode of preparation. The leaves are picked at various stages of their growth; the earlier pickings are considered the best. Green tea is classified according to the shape taken by the leaf during manufacture—Gunpowder and Hyson. In the case of the black tea, the leaves are allowed to undergo a fermentative process before baking, whereas green tea is baked directly it is picked. Tea, as sold, is nearly always blended by mixing two or more kinds with the object of securing a standard quality and flavour.

The composition of tea varies greatly with the different varieties. The following are among the chief constituents: Moisture, caffeine, tannin, albuminous matters, ethereal oil, gum, dextrin, fat, wax, chlorophyll, woody fibre, ash, etc.

The principal constituents to which the aroma, flavour, and physiological action are due are (1) the volatile oil, which is present to the extent of about 0·5 per cent., and appears to be a product of the fermentative process; (2) the alkaloid caffeine or theine (1·8 to 5·5 per cent.); (3) the tannin, which is present to the extent of 13 to 18 per cent.

While in good teas tannin and caffeine are present in fairly definite proportions (the *Lancet* suggested a combination as caffeine tannate), in cheaper teas there is either a relative excess of tannin, giving an astringent sensation, or else caffeine predominates, when a bitter taste results.

Various terms are used in the trade to describe the flavours of tea: 'herby,' 'stemmy,' 'mousy,' 'minty,' 'fishy,' 'woody,' and 'brassy' are characters not to be desired, while the 'tarry' flavour of Souchong, and the descriptions 'full-bodied,' 'toasty,' 'fruity,' 'aromatic,' 'sparkling,' 'grippy,' 'pungent,' and 'malty' apply to desirable qualities. Chinese teas are sometimes 'scented' with oleofragrans, jasmine, chloranthus, iris, rose-petals, and gardenia. According to the characters of the local water, so the varieties of tea vary in flavour with the locality, soft water rendering Ceylon tea popular, and the Indian varieties being mostly used with the hard waters.

Tea is now very rarely adulterated, on account of the provision made under the Sale of Food and Drugs Act, whereby it is examined by the Customs authorities.

Exhausted tea-leaves have been used as an adulterant; their detection is difficult, as, except when they are present in large proportion, the amount of extractive to hot water will not be of much service owing to the great variation in this figure in genuine teas. A soluble ash below 2·8 per cent. allows a presumption that exhausted leaves have been added.

Dr. J. Bell found a number of exhausted teas to give the following average figures:

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

The addition of mineral matter would be shown by the increased ash. 'Lie tea,' which may consist of sweepings, tea-dust, foreign leaves, clay, etc., has been found by Cribb to contain as much as 12 per cent. of ash.

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 too nauseous for human consumption.

Foreign leaves, such as willow, elder, sloe, hawthorn, beech, etc., are practically unknown in this country, but samples sometimes contain an undue proportion of stalk. Tea-leaves may be examined by soaking in warm water, and carefully unrolling on a tile; they can then be compared with genuine leaves. The tea-leaf has a serrated margin, an emarginate apex, and a looped venation. Microscopically, on the under surface a large number of oval stomata and (except in old leaves) long hairs are visible, while the large stone cells (idioblasts) are one of the most characteristic elements.

Ground olive-stones would be detected by their microscopical appearance (see under 'Pepper').

The facing or blooming of green tea with Prussian blue and gypsum, indigo, or anilin dyes, 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 taste of American consumers. Such 'country green' tea is now refused entry through the American Customs.

Caffeine ($C_8H_{10}N_4O_2$). — This alkaloid, formerly known as *Theine*, is identical with the active principle of coffee.

Caffeine has the following characters: Colourless, silky, acicular, odourless crystals, soluble in 80 parts of cold water, the solution having a faintly bitter taste, and being neutral to litmus. Easily soluble in boiling water, alcohol (90 per cent.), or chloroform; sparingly soluble in ether. When crystallised from aqueous solutions, caffeine contains one molecule of water. It dissolves without colour in sulphuric and nitric acids. In an aqueous solution of the alkaloid tannic acid gives a white precipitate soluble in excess of the reagent, but no precipitate is caused by Mayer's reagent or by iodised iodide of potassium—distinction from nearly all other alkaloids except theobromine.

The Analysis of Tea.—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.

Moisture.—Five grammes of the sample are dried in a platinum dish to a constant weight. The moisture in commercial teas varies from 4 to 11 per cent., the average being about 6 per cent. Tatlock and Thomson point out that on prolonged heating at 100° C., tea gains in weight; the first heating should be for not longer than one hour, and subsequent ones of half an hour each.

Caffeine (Tatlock and Thomson's Process, *Analyst*, 1910, p. 103).—Boil 2 grammes of the powdered tea, under a reflux condenser, with 800 c.c. of water, for at least an hour; filter, wash with hot water, and evaporate the filtrate to about 40 c.c. in bulk. Allow to cool, add 10 c.c. of normal solution of caustic soda, which will clear the solution, and transfer to a separator, washing in with as little water as possible, which need not be more than 10 c.c. or so. Now shake up with three successive quantities of chloroform, consisting of 40, 30, and 10 c.c. respectively. Collect the three chloroform solutions in a separator, shake up with 10 c.c. of normal caustic soda, which removes any traces of tannin, colouring matter, etc., then with 10 c.c. of water, and finally distil off the chloroform, complete the drying at 100° C., and weigh the caffeine thus obtained. If the caffeine is coloured, it may be heated in a little dilute caustic soda, and extracted again with chloroform, but if the process is carefully carried out this is unnecessary. Ammonia may be substituted for the caustic soda in the above process.

There appears some question whether a loss of caffeine occurs when it is dried at 100° C., and to be on the safe side, it is advisable to dry it in a flask and at a temperature not exceeding 95° C. (Puckner).

Total Ash.—After the estimation of moisture, the tea is ignited at the lowest possible temperature. The ash should be grey, not green. If it is greenish, it has been ashed at too high a temperature. The

total ash varies from about 5 to 7 per cent., the average being about 6 per cent.

Ash insoluble in Water and Soluble Ash.—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 c.c. 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. This should be between 2·8 and 4 per cent.

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 c.c. $\frac{N}{10}$ acid = 0·0047 K_2O. The alkalinity varies from 1·3 to 2 per cent.

Matter soluble in Water.—The tea should be first dried at 100° C., and then 2 grammes exhausted by boiling with 100 c.c. of water for an hour, filtering, and repeating the extraction till no more colouring matter is dissolved out. The extract should be from 35 to 50 per cent., calculated on the dried tea. A standard on these lines is adopted (1913) in Roumania, where an aqueous extract of not less than 25 per cent. is required. Similarly in Australia (1914), a Customs Regulation reads: 'The extract obtained by boiling the tea with 100 parts by weight of distilled water for one hour shall be not less than 30 per cent.;' the result being calculated on the dried tea.

Stalk.—This is estimated by Beeson's method: 5 grammes are boiled for fifteen minutes with 500 c.c. of water, transferred to a dish, covered with fresh water, and the stalks picked out with forceps. The Swiss Food Codex fixes the permissible maximum for stalk at 22 per cent., the Roumanian (1915) maximum for stalk being 25 per cent.

COFFEE.

Coffee consists of the seeds of the *Coffea arabica*, belonging to the natural order *Cinchonaceæ*. The ripe fruit somewhat resembles a small black cherry, the pulp of which usually contains two berries enclosed in a hard membrane-like pericarp, known as the 'parchment.' The berries are freed from pulp and parchment by drying and passing through rollers, or, as in Java, by undergoing a fermentation, after which the pulp can be washed away with water.

Coffee contains on the average 1·2 per cent. of caffeine. Another alkaloid — coffearine — is also present in the beans in very small amount, but is not extracted from the decoction by chloroform, as is caffeine. Three species of coffee grown in Madagascar are devoid of caffeine (*Analyst*, 1905, p. 399).

The coffee-berries before use are roasted at a temperature of about 450° F., to develop the aroma, flavour, and colouring matter. The characteristic flavour and odour of roasted coffee are due to an oily volatile body known as caffeol.

The analyses of two typical samples of coffee by Dr. Bell show the general composition of the coffee-berries, and the effect of the roasting process upon them (see p. 123).

In the analyses given the caffeine is probably somewhat under-estimated, an obsolete method having been employed.

The better to preserve the aroma, roasted coffee-berries are sometimes oiled with fat or coated with sugar solution. The practice is recognised, so long as it is not overdone (Roumania, 1914, requires that the weight of the coffee may not be increased by this operation by more than 1 per cent.). Other substances that have been used for glazing purposes are resin, petroleum, and shellac.

The most frequent adulterant of coffee is roasted chicory, but the following substances have been used: dandelion-root, mangel-wurzel, turnips; bean, pea, rye, and wheat flours; condemned sea-biscuit,

etc., more or less caramelised by baking and the addition of burnt sugar. In the *Analyst* (1904, p. 308) will be found analyses of three coffee substitutes made in Austria—malt coffee, fig coffee, and chicory coffee. Pearmain and Moor (*Analyst*, xx., p. 176) give an analysis of an artificial coffee. A patent has been issued for the moulding of artificial berries from a composition consisting of chicory and other adulterants. The Germans are said to use hawthorn berries and the berries of the asparagus plant as war-time substitutes for coffee.

	Mocha.		*East Indian.*	
	Raw.	*Roasted.*	*Raw.*	*Roasted.*
Caffeine	1·08	0·82	1·11	1·05
Saccharine matter ..	9·55	0·43	8·90	0·41
Caffeic acids	8·46	4·74	9·58	4·52
Alcohol extract, containing nitrogenous and colouring matters ..	6·90	14·14	4·31	12·67
Fat and oil	12·60	13·59	11·81	13·41
Albumin	9·87	11·23	11·23	13·13
Dextrin	0·87	1·24	0·84	1·38
Cellulose and insoluble colouring matter ..	37·95	48·62	38·60	47·42
Ash	3·74	4·56	3·98	4·88
Moisture	8·98	0·63	9·64	1·13
	100·00	100·00	100·00	100·00

Chicory.—The chicory plant sometimes known as the wild endive (*Cichorium intybus*) belongs to the natural order *Compositæ*. The following figures are the averages obtained by one of us (November, 1898) on nine samples of chicory:

	Per Cent.
Moisture	10·4
Total ash	5·4
Phosphates (P_2O_5)	0·4
Insoluble ash (sand)	1·9

	Per Cent.
Fat	1·8
Nitrogenous matter (N × 6·33)	8·1
Soluble extract	55·5
Specific gravity of decoction, 10 per cent.	1024·3

Chicory is sometimes adulterated with some of the substances already enumerated under the adulterations of coffee. E. G. Clayton (*Analyst*, 1904, p. 279) refers to the use of roasted beetroot as an adulterant for chicory. He states that the microscopical characters of the spiral ducts of both roots are so similar that it appears impossible to differentiate between them thus. Clayton states that the specific gravity of a 10 per cent. decoction of roasted beetroot amounts to over 1030, and the total mineral matter ranges from 6 to over 8 per cent., as against 4·5 to 6 per cent. for roasted chicory.

The Analysis of Coffee—Moisture.—Five grammes are dried at 100° C. until constant in weight. The moisture should not exceed 6 per cent.

Caffeine.—Part of the caffeine is present in the form of potassium caffeine chlorogenate which, though soluble in water, is only slightly soluble in dry chloroform. Caffeine can be estimated by Gorter's method (*Analyst*, 1908, p. 124). The percentage varies from 1·1 to 1·3.

Total Ash.—The ash is determined by igniting 5 grammes of the sample until a nearly white ash is obtained. The total ash of coffee varies from 3·5 to 5 per cent. Chicory ash is reddish owing to the presence of iron.

Microscopical Examination.—A little of the sample is boiled with water and examined with a two-thirds objective.

Coffee testa contains cells tapering at the ends not unlike a wooden paling. Chicory (and certain substances with which chicory may be adulterated) shows hollow spiral ducts never seen in coffee, the extremities of which do not taper. These are not always readily found even in pure chicory, but a clue as to the presence of the latter (or other roots)

is obtained by the presence of many particles from which the colour has been removed by the boiling with water, whereas coffee particles still retain a marked brown tint.

Estimation of Chicory.—The relative proportions of chicory and coffee in a mixture are deduced from the specific gravity of a 10 per cent. decoction. Twenty grammes of the sample are treated with 200 c.c. of water, and just raised to the boil, when the liquid is strained off through muslin. The strained liquid is then filtered through filter-paper, cooled down to 15·5° C., and the specific gravity taken with a bottle. Under these conditions, coffee gives a decoction having a specific gravity not exceeding 1009·5, while chicory gives a specific gravity of 1024·0 to 1025·0. So roughly every rise of 1·6 in the specific gravity above 1009·5 is equivalent to an addition of 10 per cent. of chicory.

Example :—

Specific gravity of coffee decoction = 1009·5.
Specific gravity of chicory decoction = 1024·5.
Specific gravity of suspected mixture = 1016·0.

1016 ⟨ 1009·5 difference = 6·5
1024·5 ,, = 8·5

15·0

15 : 6·5 : : 100 : 43·3% chicory.
15 : 8·5 : : 100 : 56·6% coffee.

Some analysts do the decoction on the dried sample, and take 1009 and 1028 as the specific gravities of coffee and chicory respectively.

Estimation of Extract (E. W. T. Jones's process).—This process is described in Johnson's *Laboratory Companion*. The decoction is evaporated and the solid matter present weighed. The sample is dried in the water-oven, and 5 grammes are weighed into a large porcelain dish. About 200 c.c. of water are added and boiled for fifteen minutes. After allowing a minute or two for settling, the liquid is strained through a piece of copper gauze placed in a funnel

into a 250 c.c. measuring flask, care being taken to disturb the grounds as little as possible. The latter are now treated with about 50 c.c. of water, boiled for five minutes, and the liquid strained off as before. The flask is then cooled, made up to the mark, well agitated and filtered, the liquid being poured on a dry filter. Fifty c.c. of the filtrate (=1 gramme of the coffee mixture) are then pipetted into a tared flat-bottomed glass dish, evaporated to dryness on a steam-bath, and finally dried in the water-oven. Treated thus chicory gives a mean percentage extract of 70, while coffee gives a remarkably constant percentage extract of 24.

Let x = percentage of chicory.
Then $100-x$ = ,, ,, coffee.
Let E = ,, ,, extract found.

$$\therefore 0{\cdot}7x + 0{\cdot}24(100-x) = E$$
$$0{\cdot}7x + 24 - 0{\cdot}24x = E$$
$$0{\cdot}46x = E - 24$$
$$x = \frac{E - 24}{0{\cdot}46}$$

Saccharine matter is frequently added to chicory. This would raise the specific gravity, and thus cause an over-estimate to be formed of the quantity of chicory present.

Starch.—A 10 per cent. decoction of the sample is boiled with animal charcoal to decolourise it, or it is treated with a solution of permanganate of potash slightly acidulated with sulphuric acid, until nearly decolourised. The decolourised decoction, after filtration, can be tested with a solution of iodine in potassium iodide, when a blue colour will indicate the presence of starch. The presence of starch would suggest the presence of breadcrumbs, acorns, rye, wheat, bean, pea, or other starch-containing substance.

It might be thought that an article sold as a mixture of coffee and chicory should contain at least 50 per cent. of coffee. Where cases in which the coffee was less than this have, after conviction

by the magistrates, been taken to the High Courts, the conviction has only been upheld when there is evidence of fraud, as when the proportion of chicory has been very excessive, or when coffee has been asked for and the price of pure coffee has been charged, but the package contained an intimation that the article was a mixture. It is very desirable that it should be compulsory for the vendor to intimate the actual percentages of the constituents.

COFFEE EXTRACTS.

By extracting coffee with boiling water and evaporating the extract to a low bulk, a coffee extract is obtained. At the bottom of the bottles of commercial extracts a considerable sediment is often to be noticed. This consists chiefly of caffeine tannate, which is insoluble in the cold, although it is easily soluble in hot water.

Analyses by C. G. Moor and Martin Priest of commercial coffee essences and extracts will be found in the *Analyst*, 1899, p. 281. These analyses show, with few exceptions, a deficiency of caffeine. Coffee extracts generally contain about 0·5 per cent. of caffeine, and the coffee and chicory extracts about 0·3 per cent. of caffeine.

Coffee extracts are adulterated with chicory extracts and saccharine solutions, such as treacle and caramel.

Salicylic acid should be looked for, as this is sometimes used as a preservative, and would be extracted with the caffeine. The extracted alkaloid should be tested with ferric chloride. Caffeine does not yield any colour with this reagent.

COCOA.

Cocoa is the prepared seed of *Theobroma cacao* and allied species, belonging to the natural order of *Byttneriaceæ*. The seeds are contained in a pulpy substance in a pod. The pods are picked when ripe,

and allowed to ferment, which renders the separation of the seeds from the pulp easy. The seeds are then dried in the sun or in ovens, after which they are roasted. This develops the aroma and flavour. After roasting, the seeds are passed through a machine which cracks them and renders the outside husk or shell easy of separation. Sometimes the shell and nib are ground together, but where the nib alone is wanted the crushed beans are passed through a winnowing machine which separates the husk from the 'nibs.'

It is claimed that, as originally made, 'cocoa' included the husk. This husk is not an indigestible fibre, but a hard, thin skin of a mucilaginous character, and, as a rule, forms from 8 to 15 per cent. of the nut. It is richer in theobromine than the nib; this tends to make it bitter and led to its intentional exclusion from cocoa by some manufacturers.

When only its own husk is present it is argued that the product is genuine cocoa. Whatever future decision may be promulgated on this point, there is no question of the impropriety of adding to cocoa already containing its own husk, further husk from other nuts.

König obtained the following average results upon eight samples of decorticated cocoa-beans and their own husks:

	Moisture.	*Nitrogenous Matters.*	*Fat.*	*Starch.*	*Cellulose.*	*Ash.*
Cocoa-beans free from shell ..	3·2	14·7	49·0	13·3	3·7	3·65
Cocoa husks ..	7·8	14·3	6·4	—	14·7	7·1

The following are the average results on eight samples of raw cocoa, after removal of the husk, by Eastes and Terry:

Moisture.	*Fat.*	*Theobromine.*	*Ash.*	*Phosphoric Acid* (H_3PO_4).
4·5	51·5	1·3	3·0	1·1

Theobromine, $C_5H_2(CH_3)_2N_4O_2$.—This alkaloid is the lower homologue of caffeine. Its amount varies from 1·3 to 1·7 per cent.

Starch.—Cocoa contains about 10 per cent. of natural starch. The granules are small and round, and are easily distinguished from any added starch with which cocoa is likely to be adulterated.

Many unreliable figures have been published on the starch content of cocoa. No reliance can be placed on those obtained by processes involving acid conversion, owing to the presence of pentosans. Some of the cellulose may also be converted to sugar. It is pretty certain that cocoa shell contains no starch (Revis and Burnett, *Analyst*, 1915, p. 429).

Fat.—The fat of cocoa, known as 'cocoa-butter,' is the *Oleum theobromatis* of the British Pharmacopœia. It is a yellowish fat, consisting mainly of stearin, having an agreeable odour and taste of chocolate. It should not be confused with coconut oil. Cocoa or cacao butter is largely used in making pessaries and suppositories, its melting-point (31° to 34° C.) being a little below body-temperature.

Commercial Cocoa.—The simplest form of commercial cocoa consists of the roasted seeds, free from husks, ground to a paste and moulded into cakes. This is sometimes known as 'rock-cocoa.' The use of natural cocoa is objectionable in some cases owing to the large proportion of fat, averaging 50 per cent., which renders it difficult of digestion.

It is impossible to powder it, so recourse is had to diluents, such as starch and sugar, or the partial removal of the fat by the process of hot-pressing. The fine pulverisation of the cocoa tissue, or the addition of arrowroot, serves to keep up the large bulk of the deposit, which otherwise would sink to

the bottom of the cup on the addition of boiling water.

'Cocoa extract' and 'cocoa essence' consist of natural cocoa partly deprived of its fat. The term 'chocolate' is generally given to preparations of cocoa mixed with sugar, starch, added cocoa-fat, etc., flavoured with vanilla.

Mixtures of cocoa with starch and sugar can be sold as cocoa if the fact that they are mixtures is disclosed on the label.

A treatment practised by some manufacturers consists of the addition of ammonia, or sodium or potassium carbonates. The added alkali emulsifies the fat, and any free fatty acid is saponified, with the result that on treating the cocoa with hot water there is less tendency for the fatty globules to separate. Such preparations are called 'soluble cocoa.'

Red sanders-wood is stated to be sometimes added to cocoa for the purpose of hiding the addition of starch (*Analyst*, 1902, p. 276), and may be detected in the microscopical examination. Iron oxide has been used for the same purpose. Arnaud has found as much as nearly 0·5 per cent. of Fe_2O_3 in a chocolate powder, and in eight other cocoa mixtures he examined found Fe_2O_3 to vary from 0·024 to 0·14 per cent. A sample of cocoa gave 0·14 per cent. of Fe_2O_3. Paul and Townley state that cocoa naturally contains a trace of copper.

Analysis of Cocoa.

Total Ash.—This is determined by igniting 5 grammes of the sample. Commercial cocoa, if untreated with alkali, usually contains 4 or 5 per cent. of ash. The total ash calculated on the fat-free sample is fairly constant (5 or 6 per cent.), provided that no treatment with alkali has taken place.

Added Alkali.—Lime is now frequently used for the alkalisation of cocoa, and it will not figure in an estimation of alkalinity made on the soluble ash, as potash and soda do. Estimates of alkalinity on the total ash are unsatisfactory; the mineral matter

tends to adsorb the indicator and the reaction is very slow. When lime is present it is necessary to digest the ash with excess of standard acid and titrate back with standard alkali.

Soluble Extract.—Five grammes of the sample are rubbed up in a mortar with 250 c.c. of cold water until a smooth mixture results. It is then shaken at intervals and allowed to stand overnight. The supernatant liquid is poured off and filtered, and 50 c.c. (=1 gramme of sample) of the *clear* filtrate are evaporated in a dish and dried to constant weight.

The cold-water extract should not exceed 18 per cent.; any material excess will probably be due to added sugar, though figures as high as 22 per cent. may be obtained with alkalised articles.

It is more satisfactory to determine this value on, or calculate it to, the fat-free dry cocoa. This eliminates the disturbing factor of variation in fat-content, and becomes a fairly constant value. Booth, Cribb, and Richards have shown that the fat-free dry nib and the fat-free dry shell both give values of about 24 per cent. for the cold-water extract.

Ash of Soluble Extract.—The residue from the above determination is gently ignited. The resulting ash should not fall below 2 per cent.

Fat.—When this is estimated in the usual manner by extracting 5 grammes in a Soxhlet extractor with ether or petroleum spirit, the process is tedious and takes sixteen hours or so. The Gottlieb process has been applied to cocoa (*Analyst*, 1906, p. 229). In commercial cocoa the fat varies from 10 to 35 per cent.

Theobromine.—Theobromine may be estimated by extracting 20 grammes of the sample with petroleum ether. After previously drying at 100° C., the residue is heated on the water-bath to free it from petroleum ether, and then extracted with alcohol (specific gravity 0·850), which dissolves sugar, theobromine, tannin, etc.; the alcohol is distilled off, the residue is taken up with water and clarified with lead acetate, and the lead is afterwards removed by sulphuretted hydrogen; from this liquid the theo-

bromine is extracted by repeated shakings with chloroform. On account of its presence in such variable proportions, it cannot be used to determine the amount of cocoa in a mixture. Further, Savini (*Analyst*, 1917, p. 84) says that part of the alkaloid is decomposed in the extraction with a solvent. Theobromine contains 31·1 per cent. of nitrogen.

Proteins.—These can be approximately estimated by determining the total nitrogen by the Kjeldahl method on 2 to 3 grammes of the sample. After deducting the amount of nitrogen due to the theobromine, the remainder is multiplied by the factor 6·25.

The total nitrogen of cocoa-nibs varies from 2·1 to 2·5 per cent., the average amount being 2·2 per cent.

Sugar.—If the sample is found to contain added sugar, 5 grammes of the fat-free sample are extracted with alcohol (specific gravity 0·850); this dissolves the sugar, and a quantity of other matters which must be removed. This is effected as detailed above; the purified sugar is inverted with citric acid and estimated in the usual way.

Added Starch.—An approximate estimation may be made by a diastase method. The taka-diastase method of Davis and Daish, as applied by Revis and Burnett (*Analyst*, 1915, p. 429), appears to offer the most consistent figures.

Fibre is estimated by the process given under 'Pepper.'

Shell.—Macara has devised a 'levigation' process, full details of which are given in Bolton and Revis's 'Fatty Foods.' Microscopically, the husk tends to be darker in colour than the nib. It shows among other characters a parenchyma of large mucilage cells, a layer of small thick-walled stone-cells, and a larger number of spiral vessels than occur in the nib. The multicellular hairs which Clayton calls 'Hassallian bodies' (frequently miscalled 'Mitscherlich bodies') occur in the perisperm, and may get eithe into the husk or the nib.

PEPPER.

Pepper is obtained from *Piper nigrum*, a perennial climbing shrub. When one or two berries at the base of the spike begin to turn red, the whole spike is pinched off; the berries are picked off and dried.

White pepper is prepared from black pepper by soaking the fruit in water to soften the husk (the dark outer layer of pericarp), which is then removed by friction. The pepper-husks have a legitimate use in the manufacture of sausages and sauces.

The chief constituents of pepper are the acrid resin, to which pepper owes its pungency; a volatile oil, which is present to the extent of about 2 per cent.; a neutral principle termed piperin, which is present to the extent of 2 to 3 per cent.; cellulose or woody fibre; and starch.

Clifford Richardson (*Bulletin U.S. Agricultural Department*, No. 13) gives the composition of black and white peppers:

	Black.	*White.*
Water	8 to 11	8 to 11
Ash	2·75 „ 5·0	1 „ 2
Volatile oil	0·5 „ 1·75	0·5 „ 1·75
Piperin and resin ..	7 „ 8	7 „ 8
Starch	32 „ 38	40 „ 44
Fibre	8 „ 11	4·11 „ 8
Albuminoids	7 „ 12	8 „ 10

Macfarlane obtained the following average figures on six samples of genuine black peppercorns and five samples of genuine white peppercorns:

	Black.	*White.*
	Per Cent.	Per Cent.
Moisture, etc., lost at 100° C. ..	12·03	12·34
Ash soluble in hot water	2·41	0·54
Ash insoluble in water	2·05	2·46
Total ash	4·47	3·0
Ash insoluble in HCl	0·36	0·55
Sand expressed as a percentage on the total ash	8·0	2·10
Alcoholic extract	8·71	7·73

After grinding, both black and white pepper are graded by bolting through sieves, which tends to cause all the mineral impurities to collect in the lower grades. During grading, the fibre tends to separate; the grades getting most of it, being grey and perhaps specky, are sold at a cheaper rate. These grades are regarded, probably rightly, by the trade as the strongest and best. However, public taste prefers a good colour, to satisfy which the 'finest' grades are bleached, it is said, with hydrochloric acid, and tinted a very pale yellow with turmeric. No trace of hydrochloric acid remains, as a washing follows, which probably removes yet more flavour and heat. Such pepper has often a musty odour in bulk, and is certainly not worth the enhanced price obtained for it.

Black peppercorns, which are much corrugated, are dried upon earthen floors, and in this process take up a considerable amount of dirt. They are frequently imported in this condition, and ground without being cleansed. The pepper prepared from such peppercorns will be found to contain a large proportion of dirt, consisting mainly of sand. There is usually a clause in 'arrival contracts' stipulating an allowance for *dust* in excess of 3 per cent.

The most frequent adulterants found in pepper are poivrette (ground olive-stones) and starch (generally ground rice), but long pepper (*Chavica Roxburgii*), linseed, gypsum, graphite, lentil-seeds, rape-seed, palm-nut powder, and spent ginger have also been detected. Imitation peppercorns made of clay are stated to have been used, while clay has also been found in considerable amount in the ground article. A fatal case of poisoning occurred through the inadvertent use of putty powder for pepper. Stoddart examined a pepper containing 10 per cent. of steatite, and also a powder sold for the purpose of improving the colour of pepper, which consisted of rice-starch, barytes, chalk, and lead chromate.

The Analysis of Pepper.—Recognition of adulterants largely depends on the microscope. The specimen to be examined should be prepared by boiling some in 5 per cent. sulphuric acid for five minutes and

then washing by decantation. It is then boiled for five minutes in a 5 per cent. solution of caustic potash, and finally washed with hot water. Black pepper when treated thus, shows portions of the husk which are characteristic. Poivrette has the following microscopical characters, as seen with a half or quarter inch objective: pale dense ligneous cells, some entire and marked with linear air-spaces, some torn and indistinct.

Rice and ground (spent) ginger are readily detected by the microscopic characters of a glycerin *cum* water-mounted specimen of the untreated sample.

Some microscopical characters of pepper hitherto overlooked are described by T. E. Wallis (*Analyst*, 1915, p. 190).

For the microscopical detection of poivrette and long pepper A. W. Stokes (*Analyst*, xiv., p. 82) warms a little of the sample with ammonia, and after washing with water examines it in a drop of glycerin with an inch power and polarised light. On rotating the prisms it is possible to obtain an entirely dark field when pure pepper is present, but no position will give a dark field when either poivrette, long pepper, or rice is present. The fragments of these latter bodies appear as faintly illuminated ghost-like fragments, the poivrette showing a distinctly reddish light, while the colour emitted by long pepper is perceptibly blue. For the success of this method the sample must be treated as described, and merely flattened out on the slide with the blade of a penknife, not ground to a fine dust.

The following figures were obtained by Campbell Brown (1887) on two samples of poivrette and a sample of ground olive-stones:

	Ash.	*Matter soluble by Boiling in Dilute Acid.*	*Matter soluble in Alkali.*	*Fibre insoluble in Acid and Alkali.*
White pepperette	1·33	38·32	14·08	48·48
Black „	2·47	34·55	17·66	47·69
Olive-stones ..	1·61	39·08	15·04	45·38

The same investigator found three samples of long pepper to have the following composition: ash, 8·91 to 9·61 per cent.; cellulose, 10·5 to 15·7 per cent.; total nitrogen, 2·0 to 2·3 per cent.; ether extract, 4·9 to 8·6 per cent.

Heisch's figures for fibre in long pepper (11·4 to 12·9 per cent.) agree closely with Campbell Brown's, but his average figure for fibre in poivrette (65 per cent.) is much higher.

D. Martelli (*Analyst*, xx., p. 181) recommends the following test for the detection of poivrette: Digest for two or three days 1 gramme of phloroglucinol in 50 or 60 c.c. of hydrochloric acid (specific gravity 1·1) and decant the clear solution. To about 0·5 gramme of the sample of pepper add enough of the reagent to cover it, and heat cautiously till fumes of hydrochloric acid begin to come off. Poivrette and like substances give a very intense and cherry-red colour.

Chevreau's reagent (1 part aniline in 3 parts acetic acid) colours pure pepper grey or white, and leaves olive-stones yellowish brown.

Neuss's test is generally to be relied on. About 2 grammes of the ground pepper are spread over a flat-bottom porcelain dish and covered with strong hydrochloric acid. True pepper turns a uniform yellow, while most adulterants remain uncoloured.

Estimation of Fibre.—Figures published for this datum vary greatly: partly because of the variations met with in commerce, partly to differences in technique. Most English workers now use the following process for determining 'fibre.' The description is that given by Dr. Bernard Dyer in the monograph on 'Feeding Stuffs' in the last edition of Thorpe's 'Dictionary of Applied Chemistry': A weighed quantity (conveniently about 3 grammes) of the ground sample, either with or without previous extraction with ether, is boiled for half an hour with 125 c.c. of a 2 per cent. solution of sulphuric acid, the loss of water due to boiling being continuously made up. The fluid is diluted with a few hundred cubic centimetres of water, and allowed to stand for some time. The bulk of the fluid is then filtered off,

any matter that becomes transferred to the filter being washed back again into the original vessel. The residue is then boiled with 125 c.c. of a 2 per cent. solution of potassium hydroxide, diluted, and filtered—this time through counterpoised filters. The fibrous matter is washed on to the filter, washed with boiling water until the washings are no longer alkaline, then with a little dilute acid, and then with water until the washings are no longer acid. It is next washed several times with methylated spirit, and, if the oil was not removed prior to the fibre determination, it must be finally washed several times with ether. Finally, the fibre is dried to constancy in a water-oven, and weighed. Instead of potash, soda may be used of equivalent alkalinity.

Stokes prefers to use acid only with pepper for fear of the cellulose being dissolved, but this treatment does not completely remove resin, etc. Whichever method is used, the results are only comparable with figures obtained in the same way. The limits given at the end of this article are for fibre estimated by the *acid and alkali treatment*.

Added mineral matter can be separated by shaking with chloroform.

The ash of genuine black pepper should never exceed 7 per cent., while it very rarely exceeds 4 to 5 per cent. Any excess is due to dirt either deliberately added, or to earthy matter which may have adhered to the berries when soft—*i.e.*, before drying. There is excuse for some extraneous matter being present for this reason in the case of black peppers, though 7 per cent. is a liberal allowance. In the case of white peppers, which are made from decorticated corns, there is no excuse for the presence of any mineral matter beyond that natural to pepper, but low-grade samples may give as much as 3·9 per cent. of ash.

Stock has drawn attention to the addition of small quantities of chalk to white pepper by the grinders, and he considers that no white pepper should be passed as genuine in which the proportion of lime (in terms of calcium carbonate) to the ash exceeds 60 per cent.

We may regard those samples as genuine which fulfil the following conditions:

	Total Ash.	*Fibre.*
Black pepper, not exceeding ..	7	10 to 18
White pepper „ „ ..	3	3·5 „ 9·5

provided that the microscopic appearance is normal. In the so-called 'finest' white pepper as sold to-day, it is usual to find only from 0·6 to 1·4 per cent. of ash, with the fibre proportionately low, about 1 per cent.

The extracts yielded respectively to ether, alcohol, and water afford no means of determining the purity of a sample, while the piperin and starch vary greatly in genuine samples. However, in dealing with adulterated pepper, it is advisable to extend the analysis, and for the interpretation of results the following standards will be some guidance.

Australian Regulations (*Board of Trade Journal*, May 25, 1917) read: 'Black pepper is dried immature berry of *Piper nigrum* L. It shall contain (*a*) no foreign substance; (*b*) not more than 5 per cent. white berries, 15 per cent. of waste material, 7 per cent. ash; (*c*) not less than 6 per cent. ext. sol. in ether and 8 per cent. ext. sol. in ethylic alcohol.

'White pepper is the dried more or less mature berry of *Piper nigrum* L. It shall contain (*a*) no foreign substance; (*b*) not more than 5 per cent. black berries, 7 per cent. of immature berries, 3·5 per cent. ash; (*c*) not less than 6 per cent. ext. sol. in ether and 7 per cent. ext. sol. in ethylic alcohol.'

CAYENNE PEPPER.

Cayenne pepper consists of the ripe dried fruit of the *Capsicum fastigiatum* and *Capsicum annuum*, belonging to the natural order *Solanaceæ*. It is also known in commerce as pod pepper and Guinea pepper.

The *Capsici fructus* of the Pharmacopœia is the dried ripe fruit of *Capsicum minimum*. It is required

to leave not more than 7 per cent. ash. Cayenne pepper is *not* a synonym for this article.

The pods of *Capsicum fastigiatum* vary from about ½ to ¾ inch in length, and are about ¼ inch in diameter, somewhat shrivelled, and composed of a smooth, shining pericarp of a dull orange-red colour, enclosing several small, white, roundish seeds. The taste and smell are both pungent and burning. The pods of *Capsicum annuum* are smaller than the above, and the powdered product is brighter in colour.

Cayenne pepper contains a red colouring matter, fat, resin, cellulose, a volatile alkaloid, and capsaicin ($C_9H_{14}O_2$), which is a colourless, highly-acrid body, soluble in ether, benzene, alcohol, and acetic acid. The total ash of cayenne pepper is generally said to vary from 4 to 6 per cent., but we have examined a sample which contained 9·4 per cent. Various adulterations are mentioned; in fact, almost anything red is said to have been used: red lead, various oxides of iron, sulphide of mercury, and brick-dust. Rice-starch has been used as an adulterant, while it is also possible that exhausted capsicum may sometimes be added.

A genuine sample of cayenne pepper should conform to the following standard:

Water should not exceed ..	..	10 per cent.
Ash should not exceed ..	..	6 ,,
Ether extract should be about	..	18 ,,

The microscopical appearance is that of a cellular structure enclosing occasional drops of oil, but no starch. The pungency for which cayenne is valued resides entirely in the matter extractable by ether, the residue left after extraction being tasteless.

Cayenne has been used for adulterating mustard and ginger. Exhausted cayenne and *Capsicum tetragonum* enter into the composition of canary foods.

GINGER.

Ginger is defined in the British Pharmacopœia as 'the scraped and dried rhizome of *Zingiber officinale*.' For flavour Jamaica ginger is most valued, but its oleo-resin content is less than the African. Spice merchants say the naturally very weak Japanese variety should not be used in ginger grinding. To prepare the root for commerce, it is either scraped and washed and dried in the sun, or it may be dried with the epidermis left on, when it is known as 'coated ginger.' There appears also to be a practice of splitting the rhizome in the case of some Japan gingers (Dyer), and gingers are sometimes dipped into boiling water to soften the outer skin. Whole ginger is sometimes whitewashed with carbonate or sulphate of calcium, to preserve it from the attacks of insects, or treated with chloride of lime to bleach it.

Ginger is frequently exhausted by immersing the whole or partially crushed rhizome in a weak mixture of alcohol and water, for the preparation of flavouring for ginger-beer. The cold-water extract, the volatile oil, and the soluble ash are reduced by this treatment, while the resin is not greatly affected.

The composition of ginger varies very greatly. Not only do differences occur in the products of different countries, but the same races of plants present considerable variation *inter se*. Ginger contains a volatile oil mainly composed of terpenes possessing the odour of ginger, but not its pungent taste.

A. H. Allen and one of us obtained the following results on some samples of known origin:

	Jamaica Gingers.				
	1.	2.	3.	4.	5.
Moisture	11·2	10·98	13·95	12·76	13·96
Ash	—	—	3·90	3·29	3·45
Soluble ash ..	1·70	1·41	3·05	1·75	1·71
Cold-water extract	15·65	13·25	14·40	12·25	11·85

	Cochin Gingers.			*African Gingers.*	
	1.	2.	3.	1.	2.
Moisture	10·64	13·50	13·23	15·97	13·70
Ash	—	3·81	3·62	3·66	3·90
Soluble ash ..	1·71	2·03	2·04	2·28	2·41
Cold-water extract	13·00	8·65	11·65	10·80	10·10

Dyer and Gilbard (*Analyst*, xviii., p. 199) point out that the alcoholic extract, after complete removal of the ethereal extract, is of value. In the gingers they examined it ranged from 2·1 to 3·8 per cent., with an average of 2·8, while in the exhausted gingers it ranged from 0·8 to 1·4 per cent., with an average of 1·2 per cent. The ash soluble in water varied from 1·9 to 3 per cent. in the genuine, with an average of 2·7, while in the exhausted gingers it varied from 0·2 to 0·5, averaging 0·35 per cent.

Turmeric is used to restore the yellow colour, and cayenne to give the necessary pungency, when these characters have been reduced in intensity by the addition of starch or exhausted ginger.

Ginger is (in this country) rarely or never adulterated with anything but exhausted ginger. Exhausted ginger possesses exactly the same appearance under the microscope as genuine ginger, as the starch cells are not altered in shape by the extraction practised.

When examined in polarised light, the unsymmetrical character of the cross in the ginger serves to differentiate it from wheat starch. The hilum and concentric rings are much less distinct in ginger starch than in potato or arrowroot starches, while the size of the granules affords an additional means of detection.

The ash of scraped gingers—that is, of all gingers except African ginger—never exceeds 4·5 per cent., unless it is raised by the addition of unnecessary dirt, or excessive amounts of substances used for whitewashing the unground rhizomes. It may be

legitimate to whitewash the unground ginger to preserve it from the attacks of insects, though many importers contrive to bring it in good condition without such means. This practice must not, however, be made the excuse for additions of gross mineral substances to ground ginger, and any sand or matter insoluble in hydrochloric above 1·0 per cent. should be regarded as an adulterant.

The external layer of unscraped ginger is about a millimetre thick; within this is the mealy portion, composed of starch granules, masses of the resins peculiar to ginger, drops of ginger oil, and fibrous matter.

In grinding ginger roots for experimental purposes, the fibrous matter very readily tends to separate from the more friable portion, and it might therefore be expected that the operations of grinding and 'grading' would cause different grades to yield analytical results, exhibiting wide differences. This, however, has been shown not to be the case by Stock (*Analyst*, xix., p. 312), who passed a sample of ground Jamaica ginger through a fine sieve, so as to cause as much separation of the fibrous matter as possible, and then examined each portion separately, as well as some of the same sample unsifted. The result showed that this treatment had very little effect on the ash (total, insoluble, and soluble), or on the potash.

Cayenne would be detected by making an alcoholic extract in the manner prescribed under 'Mustard.'

A sample of ground ginger may be regarded as genuine when it possesses the following characters:

Total ash not exceeding 5 per cent.;
Soluble ash not less than 1·5 per cent.;
Cold-water extract* not less than 10 per cent.;

and when, in addition, the histological appearance is normal.

The British Pharmacopœia requires ginger to yield not more than 6 per cent. of ash and not more

* Two grammes of sample to 100 c.c. of cold distilled water.

than 1·5 per cent. of ash insoluble in water. The latter requirement would exclude limed ginger, but the minimum cold-water extract of 8·5 per cent. admits inferior qualities.

MUSTARD.

Mustard was defined by the 1898 British Pharmacopœia as 'black mustard seeds and white mustard seeds mixed.' It has ceased to be official. The seeds of the black mustard are much smaller and only one-fifth the weight of white mustard seeds, and are dark reddish-brown in colour when of good quality. If rain occurs when they are ripening, they become greyish and lose much of their pungency.

Mustard seed when ripe contains no starch. It contains a fixed oil, which is almost devoid of taste and smell, and varying amounts of volatile oil, on which its pungent properties depend. This volatile oil (*Oleum sinapis vol.*) is an official preparation of the British Pharmacopœia, which defines it thus: 'The oil distilled with water from black mustard seeds after the expression of the fixed oil.' Characters: Colourless or pale yellow. Specific gravity 1·014 to 1·025; distils between 148° and 156° C. Dissolves readily in alcohol and ether, and to a slight extent in water. Has an intensely penetrating odour and a very acrid burning taste. Applied to the skin it causes almost instant vesication. It is required to yield not less than 92 grammes per 100 c.c. of allyl isothiocyanate when tested by the official process (see B.P.).

The ash of mustard is about 4·5 to 5 per cent., 3·8 per cent. being the lowest figure we have seen. Mustard contains about 1 per cent. of sulphur, but its presence is not sufficiently constant to be of value in determining its purity. The moisture varies from 5 to 10·6 per cent. Mucilage is present, particularly in the husk, in varying proportions.

The following figures were obtained by Clifford Richardson (*U.S. Bulletin*, xiii., 182):

	Per Cent.
Water	3 to 7·0
Ash	4 „ 6·0
Volatile oil	·5 „ 2·0
Fixed oil	31 „ 37
Starch	none
Fibre	5 to 18
Proteins	25 „ 32

Leach (*Analyst*, 1905, p. 58) gives analyses of mustard, flour, mustard hulls, and of the whole seed.

Macfarlane obtained the following figures working on genuine seed, husks, farina, and cake:

	Ash.	*Moisture.*	*Fixed Oil.*	*Extracted by Alcohol.*	*Sulphur.*	*Nitrogen.*
Mustard seed, white	4·98	6·58	27·01	15·64	1·09	4·07
„ husks „	4·42	8·20	23·66	13·74	0·88	4·42
„ farina ..	4·27	6·90	30·50	18·46	1·14	5·16
„ cake ..	7·35	7·98	14·30	15·58	1·03	5·00

Mustard is little adulterated in this country. The addition of turmeric is not generally regarded as an adulteration, but for medicinal purposes should be absent, as the 1898 Pharmacopœia gave a test for its detection.

Any addition of starch, such as is made for convenience in grinding, and for the better subsequent keeping of the finished product, is an offence under the Food and Drugs Act, unless the mustard is sold as a mixture. In the evidence taken before the Select Committee on Food Products Adulteration, it was stated that both pure and mixed mustards prepared by one firm were sold at the same price, the mixture being made, not for increasing profit, but to suit the public taste.

Mustards containing undue proportions of husk are said to find a ready sale in Germany, but not to be much used in this country.

Macfarlane and others look on the abstraction of the fixed oil as an adulteration, but as it is tasteless, and possesses none of the flavour or pungency for which mustard is valued, and renders the article more likely to become rancid, there does not appear any reason for insisting that the full amount present in the seeds should be retained. Nevertheless, an intimation of such abstraction should appear on the label. Macfarlane recommends that the lowest quantity of oil (fixed oil) that should be permitted in commercial mustard should be 30 per cent. in mustard sold as pure, and 22 per cent. in mixtures. The oil in mustards on the market appears to be very constant, twelve samples giving from 35·2 to 39·3 per cent.

Analysis of Mustard.—The sample is examined microscopically for added starch and cayenne pepper. Globules of oil are sometimes mistaken for starch granules by the inexperienced. If any doubt be felt, the slide containing the sample mounted in water should be taken, and close to the edge of the cover-glass a drop of dilute iodine solution should be placed. A piece of filter-paper is applied to the opposite edge of the cover-slip, when the iodine will be sucked through on to the specimen, and on again looking at it through the microscope the granules of starch will be found coloured black.

Starch can be detected by mixing with a considerable amount of water in a small beaker and adding excess of iodine solution. The starch stained deep blue or black will sink to the bottom. Iodine is absorbed with avidity by the volatile oil and less quickly by the fixed oil; an excess beyond the iodine put out of action by oil is required to bring off the test.

If starch is seen, it can be estimated by conversion into sugar; but this must be preceded by treatment with ether and proof spirit (Allen), or the result will be invalidated owing to the production of sugar from some of the substances natural to mustard.

If turmeric is present, an orange-red colour is produced on the addition of ammonia. Turmeric may also be tested for by digesting 2 or 3 grammes

of the sample in strong spirit and filtering. Through the filtrate a piece of white filter-paper is drawn and allowed to dry. This is moistened with very dilute HCl, and then dipped in a cold aqueous solution of boric acid. If turmeric is present, an orange-red colour is produced, turning blue or green on the addition of caustic soda.

To detect cayenne, which might be added to give pungency to an adulterated sample, a little of the mustard should be boiled for a few minutes with alcohol, and the filtered extract evaporated to dryness at 100° C. Cayenne would be detected by the pungent taste of the extract, and by the production of the characteristic acrid fumes of cayenne on the extract being heated. Genuine mustard gives a smell suggestive of kippers frying.

SPICES.

Spices are liable to many gross and varied forms of adulteration. Cloves and caraway seeds are exhausted of their essential oil, the resulting 'drawn' or 'spent' samples being used to adulterate genuine samples. The substitution of a cheaper spice for one of higher value is frequent, as in the case of pimento for cloves, cassia for cinnamon, etc. In addition, powdered spices are adulterated with refuse of all kinds: Sand, gypsum, ground walnut and coconut shells, ground olive-stones, exhausted ginger, pepper refuse, mustard husks, biscuit dust, various forms of farina, damaged macaroni and vermicelli.

The following are the characters of the more important spices:

Caraway Seeds.—These are derived from the dried fruit of the *Carum carui* (natural order *Umbelliferæ*), and occur in commerce in the form of separated mericarps.

The Russian fruit is less carefully collected, and contains a larger amount of ash than the English, Dutch, or German fruits. The Russian fruit in its powdered form appears to be chiefly used for veterinary purposes.

After caraways have been distilled for oil and subsequently dried very little alteration in appearance is observed, but the ether extract would be thus considerably reduced from the 10 per cent. that whole caraways yield. Caraways yield about 5 per cent. of oil, and the ash varies from 5·5 to 7·5 per cent. The British Pharmacopœia allows a liberal ash; not exceeding 9 per cent.

Cinnamon and Cassia.—These spices are the barks of several species of the genus *Cinnamomum*, the true cinnamon being a native of Ceylon, where it is largely cultivated, and the cassias being derived from several other species growing in China, India, and the East Indies. Cinnamon consists of the true bark, or *liber*, of *Cinnamomum zeylanicum*. The crop is gathered about May and November, the two-year-old shoots being stripped and slightly fermented.

Cinnamon as it reaches the market is very thin, the outer and inner coats of the bark having been removed. Cassia, on the other hand, is thick, as it consists of the entire bark, and can be distinguished by its retaining its natural outer surface. Cinnamon is far more valuable than cassia, as there is a smaller supply, and intrinsically it contains a much larger proportion of volatile oil, and that of greater and more delicate aroma. In consequence, cassia is largely substituted for cinnamon.

Powdered cinnamon is extensively adulterated with ground walnut-shells (Dyer and Gilbard, *Analyst*, 1895, p. 129). Stock (*Analyst*, 1897, p. 253) found cassia adulterated with exhausted ginger, and very abnormal amounts of mineral matter.

Cinnamon contains from 0·5 to 1 per cent. of essential oil, the total ash averaging 5·5 per cent. The British Pharmacopœia stipulates for an ash not exceeding 5 per cent.

Cinnamon contains starch, the granules being very small and chiefly oval in shape.

Cloves.—Cloves are the dried calyx and flower-buds of *Eugenia caryophyllata*, an evergreen tree belonging to the myrtle order. Their valuable properties are due to the volatile oil, the best having as much as 16 per cent. Removal of the oil before grinding is

the commonest method of deception. The addition of the cheaper clove-stems is also practised. The microscope reveals their presence by certain cells which they contain, which are absent in the bud.

Exhausted cloves when whole are easily detected by their shrivelled and striated appearance, while the ash is raised slightly and the ether extract reduced considerably.

The ash of cloves should not exceed 7 per cent. (B.P.), and the total ether extract should be about 20 per cent.

Pimento is sometimes substituted in part or entirely, as eugenol has a clove-like flavour. The coarser adulterants, mineral matter, coconut shells, flour, peas, and the like, have seldom been observed.

Nutmeg and Mace.—These spices are different portions of the fruit of *Myristica fragrans*, which grows principally on the Banda Islands, the nutmeg being the kernel, and the mace one of the outer coats, or *arillus*. When ground they are mixed with diluents of various descriptions, principally cereals and their refuse, which are easily detected. Owing to the infrequency of the sale of the powdered nutmeg and mace, their adulteration has attracted but little attention.

The long nutmeg is the produce of *M. fatua*. The nutmeg contains about 8 per cent. of an aromatic and pungent essential oil. Mace contains about 4·5 per cent. of essential oil.

We have not met any specimens of nutmeg giving more than 3 per cent. of ash.

The ash of mace should not exceed 6 per cent. Mace is adulterated with Bombay mace, and when this is present the alcoholic extract (which is red or yellow in colour) gives a red precipitate with basic acetate of lead, while true mace gives a white precipitate. Turmeric would give a similar reaction, but can be detected by the boric acid test (Holmes, *Analyst*, 1909, p. 21).

The petroleum ether extract of Bombay mace is much the same as that of Banda mace, but Messrs. Southall Brothers, and Barclay show that if, subsequent to the petroleum ether extraction, the sample

is extracted with ether, the latter extracts say 35 per cent. from Bombay mace against say 1·7 from true Banda mace.

Under the microscope, true Banda mace is white or greyish relieved by occasional pale yellow masses and fragments of brownish wood fibre. Bombay mace, on the other hand, shows deep red resinous masses from the oil glands of its outer layers and bright yellow lumps from the deeper strata.

Pimento, or Allspice.—Allspice, or pimento, is a small dry berry, the fruit of *Pimento officinalis*, an evergreen tree of the myrtle order common in the West Indies. Pimento contains starch and about 4 per cent. of an aromatic pungent oil much like that of cloves. Our supplies come wholly from Jamaica. The ash should not exceed 5 per cent.

HONEY.

Honey consists of the saccharine substance collected by bees (*Apis mellifica* and *A. dorsata*) from the nectaries of flowers, and deposited by them in the cells of the honeycomb. Honeydew, a secretion of the leaves of various trees and plants, is also gathered by bees.

The essential constituents of honey are dextrose and lævulose. A solution turns the plane of polarised light to the left, which property furnishes a method for the detection of the adulteration. But honey is sometimes dextro-rotatory; this may be due to the bees having been fed on sugar-syrup or by their having gathered honeydew.

Honey varies according to the plants from which the nectar was obtained, the difference in the aromatic constituents altering the taste and aroma of the honey. Owing to its being gathered from poisonous plants, honey has caused poisoning.

In the conversion of nectar into honey the water is reduced from about 75 to 20 per cent. through the heat of the hive, through the bees fanning it with their wings, and by a process of regurgitation. The

bee secretes enzymes, diastase, and invertase, which have the power of inverting starch and sucrose.

The colour depends on the flowers and season. White-clover honey is almost water-white, while that from golden rod may be nearly black. The colour becomes darker as autumn advances.

Genuine honey on microscopical examination will always show the presence of pollen grains. When honey is specified as being derived from a particular source, the pollen grains should be examined to ascertain whether they are identical with those from the plant named. Pollen grains would generally be absent from a filtered honey.

Honey is largely adulterated; the substances generally used are glucose, starch paste, low-grade malt extract, and cane-sugar. The first, on account of its low price, is the most common, and, mixed with enough of the genuine article to give it a flavour, is 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.

To increase the yield of honey, bees are sometimes fed on saccharine solutions, which practice in some countries is regarded as adulteration. It is rare for sucrose to exceed 6 per cent. in natural honey, 1 to 3 per cent. being the usual finding.

It is said that formic acid occurs in honey. If so, it is not invariably present.

Examination in the Saccharimeter.—For description of the instrument see monograph on 'Sugar.' On the sugar scale honey will indicate from −4 to −15. Seldom, however, as low as −15. Owing to the high dextro-rotatory power of glucose,* a com-

* When 'glucose' is referred to as an adulterant of sugar foods, it is not pure dextrose that is thought of, but the commercial glucose that consists principally of dextrose, but also contains maltose and varying quantities of dextrin. Maltose and dextrin are both much more dextro-rotatory than is dextrose. Commercial glucose is prepared by boiling starch with dilute acid (sulphuric acid was, and hydrochloric acid is, usually used); the starch is first converted into dextrin and then into dextrose: hence the presence in commercial glucose of dextrin (*i.e.*, incompletely

paratively small amount will neutralise the lævo-rotatory power of the honey. The same, of course, is true if cane-sugar syrup is added. 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.

The mode of procedure is as follows: 26·048 grammes, or whatever is the 'normal' weight for the instrument used, of the honey are taken, dissolved in a flask of 100 c.c., and the solution filtered through a small quantity of bone black to clarify it. A tube of 200 millimetres is then filled with the solution and placed in the instrument which is 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 further differentiation is necessary. This is accomplished as follows: A solution is prepared as stated, or 50 c.c. 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, neutralised with sodium carbonate or sodium hydrate, and re-polarised. 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 lævo-rotatory, and which is termed

hydrolysed starch), sulphates (or chlorides) from the acid used, and sometimes arsenic from impure acid. Some maltose is also found. The rotation of commercial glucose varies, largely according to the amount of dextrin present. Bodmer, Leonard, and Smith (*Analyst*, 1899, p. 252) took the specific rotation of glucose syrup as $[a]_D = +110°$. This article must be distinguished from invert sugar, though the latter is sometimes referred to as 'glucose.' Invert sugar is formed by the hydrolysis of cane-sugar and consists of equal parts of dextrose and lævulose. Lævulose turning the plane of polarised light more to the left than dextrose does to the right, invert sugar is lævo-rotatory; its specific rotation is $[a]_D = -20·5°$.

invert sugar, and acts in the same manner as honey.

Temperature has more or less effect on the rotatory power of invert sugar; consequently all the readings should be at a uniform temperature in order to obtain a proper comparison. It is usual to read invert sugar at 15·5° C., at which temperature its $[a]_D$ is $-22°$.

The **Water** in genuine honey varies from 15 to 25 per cent.

Ash.—This varies from 0·03 to 0·4 per cent. O. Hehner (*Analyst*, x., p. 217) states that the ash of genuine honey is always alkaline, whereas that of artificial glucose is invariably neutral. The ash of genuine honey contains manganese, phosphates, and sometimes borates.

Acidity.—This is returned, sometimes in terms of formic acid (0·03 to 0·20 per cent.), sometimes as c.c. normal alkali required by 100 grammes (0·6 to 6·0 c.c.). Litmus paper is said to be the best indicator.

Paraffin-Wax.—Artificial comb consisting at least partially of paraffin-wax is extensively in use. 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 carbonisation.

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.

Glucose.—This is detected in the polarimetric examination. 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, or calcium chloride, common impurities in commercial glucose.

Invert Sugar.—Fiehe's test depends on the presence of α-hydroxy-δ-methylfurfuraldehyde in all artificial

invert sugar. As modified by Georges Halphen, a positive reaction for invert sugar consists in the production of a bright red colouration when 2 c.c. of an ethereal extract of the honey are treated with 2·5 c.c. of absolute alcohol, 0·3 c.c. of hydrochloric acid, and 0·02 gramme of resorcinol. The bright red colouration is also yielded by certain essential oils and other aldehydic substances. If present, these may be removed by a preliminary extraction of the honey with light petroleum; the furfuraldehyde compound remains insoluble in this solvent and may be extracted subsequently by treatment with ether.

A serological test devised by Langer (abst. *Analyst*, 1910, p. 165) depends on a precipitin reaction yielded by the proteins of a sample when mixed with a serum from rabbits injected with honey proteins. It is now claimed that the test is roughly quantitative in its indications, but this would not seem the case when honey had been centrifugally separated from the comb, as such honey contains little albumin and consequently yields little precipitate.

Purified honey (*Mel depuratum*) is official in the Pharmacopœia. It must have a specific gravity of 1·36; the optical rotation of a 25 per cent. w/v solution after decolourisation by animal charcoal must be between 0° and −5° at 15·5° C. in a 200 millimetre tube; must be free from starch and contain not more than traces of chlorides and sulphates; must not leave more than 0·25 per cent. of ash. The Pharmacopœial requirement that the solution of the ash in distilled water should not be alkaline to litmus, precludes genuine honey and would mark a preference for adulteration with starch or invert sugar; *vide* Hehner (*ante*).

SUGAR.

Commercial sugar is obtained from the sugar-cane (*Saccharum officinarum*) and from the white beet (*Beta maritima*). The sugar-cane yields from 10 to 20 per cent. of sugar, and the beetroot nearly as much. Sugar, as derived from the cane, consists of sucrose

($C_{12}H_{22}O_{11}$), together with a small quantity of glucose, or 'invert sugar.' That obtained from beetroot also consists of sucrose; normal beetroot sugar is free from glucose. Sucrose forms large monoclinic prisms, and exercises a powerful dextro-rotatory action on a ray of polarised light. When sucrose is heated above 160° C., it is converted into an amber-coloured body known as 'barley-sugar,' which consists of a mixture of dextrose and lævulose. At a higher temperature a reddish-brown substance is formed, known as caramel. Sucrose is soluble in half its weight of cold water, and in all proportions in boiling water.

Sugar is met with in commerce in all conditions of purity, from the brown or 'moist' sugars to the almost absolutely pure sucrose sold as 'loaf sugar,' 'white crystals,' etc.

Moisture.—Heat 5 grammes in air-oven at 105° C. until the weight is constant (about two hours).

Raw sugars contain from 0·5 to 6 per cent.; refined sugars below 0·5 per cent. of moisture.

Total Ash.—Five grammes of the sample are ignited, preferably in a muffle, after moistening with pure concentrated sulphuric acid. The ash is white in about twenty minutes, and nine-tenths of the sulphated ash is taken as true ash. The ash of sugar consists of silica, alumina, lime, salts of potash and soda, and varies from a trace to about 2 per cent.; brown sugar sometimes contains an undue proportion of sand.

Glucose.—Reducing sugar is estimated by one of the modifications of the Fehling solution given below. Raw sugar should not contain more than 2 per cent. and refined sugar not more than 0·1 per cent. of glucose.

Advantage is taken of the optical rotation of cane-sugar for its estimation. The 'polarisation,' as it is termed, is employed in all commercial transactions and for the assessment of duty by customs.

The Polarimeter.—The specific rotatory power of a body, usually expressed as $[a]_D$, is the amount of angular rotation in degrees of the ray of polarised light which is produced when a solution of the sub-

stance, containing 1 gramme in 1 c.c., is examined in a column 1 decimetre long. It is expressed by the following formula:

Let a = the observed angle, c the strength in grammes per 100 c.c., and l the length of the tube used in decimetres; then—

$$[a]_D = \frac{100a}{c \times l}$$

A solution of 10 or 20 grammes of sugar per 100 c.c. is made, and the rotation taken. $[a]_D$ for sugar is $+66{\cdot}6°$, and the amount of sugar may be determined by substitution in the formula.

Polarimetric measurements are usually given in degrees of arc (*i.e.*, angular degrees) for a tube of 20 centimetres at a temperature of 20° C. with reference to yellow light (D).

The best form of instrument is one of the half-shadow type, for use with the sodium monochromatic light. This, destroying all colour, causes a dark shadow to appear when the instrument is used. Colour-blind persons use it without difficulty.

Saccharimeters are polarimeters adapted by special graduations for use with sugar. Each make of instrument has its own 'normal weight' of sugar—*i.e.*, the amount of sucrose dissolved in water and made up to 100 c.c., which produces a deviation of 100 divisions on the sugar scale when examined in a 200-millimetre tube. The normal weight of the Laurent instrument is 16·19 grammes, while the Soleil Scheibler and the Schmidt and Hansch instruments require 26·048 grammes. We believe that recent instruments of all brands are made for a standard 'normal weight' of 26·048 grammes. Sugar degrees of such instruments are converted into angular degrees by multiplying by 0·3469.

Using 'normal weights' and a sugar scale, pure sucrose, as stated above, will read +100. The commercial glucose, when the normal weight is used, will indicate from 155 to 170 to the right (or *plus*) according to the greater or lesser amount of dextrin present.

Before a coloured sugar (West Indian, treacle, and

molasses) can be polarised, the normal weight having been dissolved, it is clarified with basic acetate of lead, and then made up to 100 c.c. The remainder of the technique is described under 'Honey.'

Fehling's Method.—Fehling's solution is made as follows: 34·64 grammes of pure crystallised sulphate of copper are dissolved in distilled water and the solution diluted to 500 c.c. Seventy grammes of caustic soda and 173 grammes of recrystallised potassium sodium tartrate (Rochelle salt) are dissolved in about 100 c.c. of water, and the solution diluted to 500 c.c. 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 c.c. of this mixed solution:

0·0500 gramme dextrose, lævulose, or invert sugar.
0·0475 gramme cane-sugar (after inversion).
0·0678 gramme lactose.
0·0807 gramme maltose.

Fehling's solution can be used in two ways: as a volumetric solution, in which the sugar solution is run from a burette into a quantity of the Fehling's solution until all the copper in the latter has been reduced, when, knowing the amount of specific reducing sugar which was necessary to effect this, this will, of course, be the amount of this sugar run into the Fehling; and as a gravimetric estimation by adding to an excess of boiling Fehling solution a quantity of sugar solution insufficient to reduce all the copper, filtering off the cuprous oxide, washing, drying, and either weighing as the black oxide or reducing to metallic copper.

The Volumetric Process.—In former times the end-point of the reaction was taken as when all blue colour had disappeared from the boiling liquid. Correct results are not easily obtained in this way, and it is better to employ some indicator to ascertain the end-point. Such an indicator is not added to the liquid, but 'spotted' on a tile. A useful indicator is made as follows: 0·05 gramme starch is boiled with a few cubic centimetres of water, 10 grammes potassium iodide added, and then made up to 100 c.c.

This needs to be freshly prepared ('Harrison's Indicator,' *Analyst*, 1903, p. 298).

The article to be examined is dissolved or diluted so that the solution contains about 1 per cent. of the reducing sugar, and placed in a burette; then 10 c.c. of the mixed Fehling solution are placed in a flask, 40 c.c. of water added, and brought to the boil. About 20 drops of the starch and potassium iodide paste are 'spotted' on a tile. The liquid is run cautiously from the burette until the end-point is nearly reached—having regard to the fact that if using lactose solution the reduction takes longer than when glucose is being estimated—then the additions from the burette are made very gently, and from time to time a drop of the liquid from the basin or flask is taken out (precipitate and all) and placed on top of a 'spot' on the tile, on top of which a drop of acetic acid is placed. The 'spots' will develop a blue colour till all the copper is reduced. A second, and perhaps a third, estimation should be made, in order to attain the end of the reaction with the minimum of delay.

Instead of Harrison's indicator, that of Ling and Rendle can be used: One gramme of ferrous ammonium sulphate and 1·5 grammes of ammonium thiocyanate are dissolved in 10 c.c. of water at a moderate temperature and immediately cooled; 2·5 c.c. of concentrated hydrochloric acid are then added. The solution at this point will have a brownish-red colour owing to the invariable presence of a ferric salt. This is reduced by shaking the reagent with a little zinc dust. Ling and Rendle's indicator is 'spotted' on a tile and the end-point of a titration is reached when a drop of the mixture of Fehling solution and sugar ceases to give a red colour with a drop of the indicator.

It is advisable to standardise Fehling solution personally. One gramme of pure cane-sugar is dissolved in 100 c.c. of water and inverted by heating with 10 c.c. concentrated hydrochloric acid at 70° C. for ten minutes. After neutralisation with sodium hydrate in faint excess, the liquid is made up to 200 c.c. Ten c.c. of Fehling solution diluted

to the extent to be adopted with the sample and using the same indicator are titrated with this solution and the factor established.

Soxhlet's figures for working with a 1 per cent. solution of sugar are as follows:

50 c.c. of undiluted Fehling are reduced by—

0·2375	gramme	of	glucose.
0·247	,,	,,	invert sugar.
0·2572	,,	,,	lævulose.
0·338	,,	,,	lactose.
0·389	,,	,,	maltose.

When 10 c.c. of Fehling are diluted as mentioned above, this quantity is reduced by—

0·0495	gramme	of	glucose.
0·0515	,,	,,	invert.
0·0538	,,	,,	lævulose.
0·0676	,,	,,	lactose.
0·0741	,,	,,	maltose.

The Gravimetric (O'Sullivan's) Process.—A quantity of Fehling solution (20 c.c. or 50 c.c.) diluted with an equal bulk of water is brought to the boil, and a measured quantity of the sugar solution is run in, and the boiling continued for another two minutes (for lactose six minutes). At the end of this time there should be a red precipitate, and the liquid should be still blue. If the liquid is colourless, the experiments must be repeated, using less of the sugar solution. The cuprous oxide is filtered off, well washed with hot water, and then ignited, gently at first, in a platinum crucible. The black copper oxide is weighed, and the weight multiplied by 0·4535 gives the weight of the glucose in the sugar solution added. The method is open to the objection that CuO is hygroscopic and easily reduced by filter-paper.

A correction for the copper withdrawn from solution by the filter-paper and for that spontaneously reduced is determined. This usually amounts to 2 milligrammes, and is deducted from that found.

Many modifications of this process are in use. One

frequently used requires the addition, to the hot undiluted Fehling solution, of the sugar and sufficient boiling water to bring the total bulk to twice that of the undiluted Fehling. The heating is sometimes done on a boiling water-bath, the heating being continued for fourteen minutes after addition of the sugar solution.

Filtration through asbestos fibre is often recommended, but alkaline copper solutions extract appreciable weights from asbestos and a preliminary washing with caustic soda solution does not always entirely remove the objection. This modification requires much practice before reliable results are obtained.

Foreign Colouring Matter.—Beet-sugar crystals are coloured with anilin dyes and sold as 'Demerara' sugar. The presence of a dye is no proof that a sample is not West Indian sugar, as these are frequently coloured.

Dyed samples will generally turn pink on the addition of hydrochloric acid to the sample. The suspected sample should be extracted with absolute alcohol. This will, in the case of dyed sugars, extract the foreign colouring matter, leaving the sugar crystals colourless. The natural colouring is not extracted by this treatment. A skein of wool, preferably slightly mordanted with aluminium acetate, is dipped into the solution, and warmed for some time in the water-bath, well washed, and dried. The skein will be dyed of a more or less marked yellow colour if artificial dyes are present. In the case of dyed sugar, the crystals, on examining with a lens, will generally be found to be very unequally coloured.

Beet-sugar is bleached by passing it through bone-black, or by the application of sulphur dioxide, the latter process being also commonly used for clarifying cane-sugar. Both forms of sugar are treated with lime to remove acidity and carry down impurities. Chloride of tin was formerly employed to fix the colouring matter of the natural cane-sugar, while ultramarine or dyes of the methyl-violet class are sometimes added to the white sugars to improve

their appearance. Ultramarine can be detected by making a solution of the sugar and allowing to settle, or by examining a considerable number of the sugar crystals with a lens.

In Anderson *v.* Britcher, a King's Bench decision found that 'Demerara sugar' had become a conventional term, and could properly be applied to sugar grown in the West Indies and Mauritius, when, except for place of origin, it was a similar article. The article in question had been dyed with an organic dye.

JAM.

Webster defines jam as 'a conserve of fruit, boiled in mass with sugar and water.' Sugar in this definition refers to the forms of sucrose—beet, cane, and sorghum. Glucose is sometimes added to prevent crystallisation on cooling, and although inferior to sucrose both in price and sweetening power, its addition has been held justifiable by the High Court, even when present to the extent of 13 per cent. Lemon-juice is added for a similar purpose. Certain jams, when first prepared, are deficient in pectinous material, and instead of boiling to a lower bulk, the consistency is sometimes attained by the addition of apple-pulp, apple-juice, gooseberry-juice, carrots, or mangel-wurzels. A jelly is thus produced without the fruit being broken up. Arnaud has pointed out that frequently the refuse from cider-presses or the parings from canning establishments is used. When such are employed, the argument that no cheapening of the product is obtained is untenable. Gelatin may also be used for thickening. Fruit other than that designated on the label is sometimes incorporated. This is particularly liable to occur in a bad year for certain fruits, when, in spite of an augmentation in the price of the respective jams, the demand is in excess of the supply. Paper impregnated with preservative is sometimes laid on top of the jam, as a protection from mould.

The sugar acts as an antiseptic, and preservatives would appear to be unnecessary. The Depart-

mental Committee on Preservatives and Colouring Matters recommended that salicylic acid be not used in a greater proportion than 1 grain per pound of solid food. It is seldom found in so small a quantity in jam, the usual proportion being about 3 grains per pound.

Fictitious raspberry jam has contained wooden pips. In a well-made jam from this fruit the number of pips is remarkably constant. Arnaud gives it as 200 per 10 grammes. Such a count must not be taken as any criterion of purity, because the material expressed from the fruit for raspberry jelly or wine may be replaced by a similar amount of gooseberry-juice, apple-pulp, or other filling.

Moisture.—In the estimation of moisture the expulsion of water is a matter of difficulty. It is preferable to estimate the sugar present, add 5 per cent. for fibre, etc., and subtract the sum from 100. Arnaud gives 26 per cent. as the average.

Apple-pulp is detected by a microscopical examination showing parenchymatous tissue occurring in apple and other adulterants, but this should not be confused with the pulp cells found in the fruits themselves. Some closing of the diaphragm on the substage or condenser of the microscope is needed to see the parenchyma.

Unsound Fruit.—The microscopical examination should include work with a one-sixth objective, when large numbers of yeast cells will be seen if the jam has been made from fermented pulp, and many fragments of mycelia and spores of moulds if mouldy material has been used. Especially in plum jam, it is difficult to differentiate mould spores from the elements of the pulp cells. Gram's method of staining (see 'Aids to Bacteriology') can be used. Yeast cells and most of the mould spores retain Gram stain, while the round chromoplasts of the pulp cells do not. To obtain the material in a form suitable for staining, we have devised the following process: 10 grammes are mixed with 100 c.c. of tepid water and strained through a tea-strainer. The liquid is left for, say, two hours to allow subsidence of the bulk of the fruit débris, and some of the top liquid is centrifuged.

The deposit contains the concentrated yeast cells and mould spores.

Gelatin.—A little tannin added to the filtered hot-water extract will throw down a precipitate if gelatin is present. Gelatin may also be detected by adding to 10 c.c. of a 10 per cent. solution about 5 drops of lead subacetate solution, filtering through cotton-wool, adding sulphuric acid to form lead sulphate with the excess of lead, and again filtering. Barium carbonate is added to neutralise excess of acid, and after again filtering, an equal bulk of saturated picric acid is added to the filtrate. A yellow precipitate is immediately produced in the presence of gelatin (Stokes' test). A similar precipitate will be produced if the lead has not been entirely removed.

Agar-agar.—The jam is mixed with dilute sulphuric acid and potassium permanganate added to destroy the organic matter. The residual liquid is centrifuged, and the deposit examined for the diatoms always present in agar. The gel-producing power of agar being quite ten times that of gelatin, little is likely to be required, and the search for diatoms should be prolonged. T. Macara has made this a less protracted business by gently igniting the residue, which destroys the organic débris without injury to the diatomaceous fabric.

Salicylic Acid.—For the estimation of salicylic acid, 2 grammes of the jam may be warmed with a small quantity of water acidulated with sulphuric acid, and the liquid, after cooling, filtered into a separating funnel. The residue is extracted two or three more times with warm acidulated water, each lot of liquid being poured through the filter into the funnel after cooling. The liquid in the separating funnel is shaken up with an equal volume of ether, and the aqueous liquid run into a second funnel, where it is shaken with a second lot of ether. The aqueous liquid may be shaken with a third lot of ether, but this is seldom necessary. The ether extracts are mixed, washed once with a little water, and then are shaken with about 20 c.c. of distilled water containing 1 c.c. of a 1 per cent. solution of iron alum. When separated, the aqueous liquid is

run into a Nessler cylinder, and the ether is agitated with 10 c.c. of distilled water containing 0·5 c.c. of iron alum solution, which, when separated, is added to the coloured liquid in the Nessler cylinder. The ether is shaken with a third portion of distilled water and iron alum which, if coloured violet to a perceptible extent, is added to the previous violet extracts, and the total extracts made up to 50 c.c. with distilled water. The colour is matched against a standard salicylic acid solution, which is treated with a similar volume of ferric alum solution, and made up to 50 c.c. The standard salicylic acid solution is conveniently prepared by dissolving 0·1 gramme of salicylic acid in a little alcohol and making up to 100 c.c. with distilled water. For use, this solution is diluted with nine times its volume of distilled water, and each c.c. of the weak solution contains 0·0001 gramme of salicylic acid. It should not be more than a few days old. After comparison, further quantities of iron alum solution should be added to both sample and standard to make sure that the maximum colour has been reached in each case, and should the colour amount to more than 8 or 9 c.c. of the standard, a suitable quantity of the coloured liquid of the sample must be diluted to 50 c.c. and matched. Volume of the liquid and amount of ferric solution must be the same in both sample and control. Where it is not likely that so small a quantity of jam as 2 grammes will be representative, as with plum jam, a larger quantity of 10 or 20 grammes must be extracted with acidulated water, and an aliquot portion, representing 2 grammes of the sample, used for the ether extraction.

The use of sulphuric acid for liberating salicylic acid from combination and of ferric ammonium sulphate were first suggested by Sidney Harvey.

Benzoic Acid.—For the detection of benzoic acid, an acid aqueous extract similar to that described above is shaken with a mixture of ether and petroleum ether as described on page 46.

The Massachusetts State Board of Health recommend the following procedure: Extract the acidified sample with ether, add ammonia to the ether extract

in excess, and evaporate to dryness in a large watch-glass. Fasten with clips or otherwise another watch-glass of the same size above it, thereby forming a double convex shell, a sheet of filter-paper being preferably interposed between the two glasses, and heat the lower watch-glass on a small sand-bath, or over a small flame. If present, crystals of benzoic acid sublime on the upper watch-glass, where they may be recognised under the microscope; or they may be dissolved in dilute ammonia, the solution evaporated to dryness, the residue taken up with a small quantity of water, and a few drops of neutral 0·5 per cent. ferric chloride are added, when a brown precipitate will be produced if benzoic acid be present. Ferric chloride may be made neutral by the addition of a little ammonium carbonate, warming nearly to boiling, and filtering.

In searching for preservatives it should be borne in mind that formaldehyde is said to be produced in small quantities from the sugar during the process of boiling. The Montana Experiment Station analysts and Duckwall have shown that many fruits contain naturally salicylic and benzoic acids. Whortleberries contain 0·6 to 0·8 gramme of benzoic acid per litre, while the following amounts of salicylic acid (stated in milligrammes per kilo of fruit) were found: currants, 0·57; cherries, 0·40; plums, 0·28; crab-apples, 0·24; grapes, 0·32.

TABLE JELLIES

Colonel W. W. O. Beveridge (*Journ. R.A.M.C.*, January, 1911) gives the composition of granulated jelly powders as: gelatin 13 to 17 per cent.; sugar about 80 per cent.; tartaric or citric acid from 1·5 to 2·5 per cent.; flavouring and colouring matters. He says that no preservatives are allowable; sulphites, salicylates, and benzoates should be looked for.

Cochineal, caramel, and saffron are the best colours, but anilin dyes are sometimes used.

Acidity reduces the setting power of gelatin (T. Thorne Baker, *Medical Press*, July 17, 1907). Be-

veridge (*loc. cit.*) found a jelly having an acidity of 0·35 per cent. (as acetic acid) to set at ordinary temperature; one with acidity equal to 0·54 per cent. to require ice; and one with 0·71 per cent. acidity to keep liquid at all temperatures down to 0°.

ICE-CREAM

Ice-cream should be made from milk, cream, and sugar, with or without eggs. Such an article will contain from 8 to 14 or more per cent. of milk-fat. However, a much inferior article is commonly sold as ice-cream in this country, containing only 2·5 to 3 per cent. of milk-fat and no eggs, and is made thus: 'Ice-cream powder' is mixed with a little milk to a smooth paste and a mixture of hot sugar and milk poured over it. The product, after cooling, is frozen. 'Ice-cream powder,' also called by other more or less inappropriate names, is simply maize and/or arrowroot starch coloured with an anilin dye and flavoured with vanilla or a 'fruit-flavour.'

Gelatin, gum tragacanth, and agar-agar are sometimes used as 'fillers'; their presence is undesirable. It is to be feared that thawed ice-cream is often refrozen and sold—a dangerous practice. We have never found preservatives in ice-cream, but they should always be looked for.

Rarely is ice-cream free from traces of the poisonous metals. Usually zinc is present in amounts of from 0·02 to 0·06 grain per pound, occasionally more. Part of this may come from milk-churns, but probably the galvanised 'freezers' yield most. Lead is sometimes to be found.

CUSTARD POWDER

Custard powders are sold as substitutes for eggs in the preparation of custard. Since they generally consist of maize starch and/or arrowroot, flavoured with a little vanilla, coloured with a coal-tar dye, they form very unsatisfactory substitutes for eggs.

LIME AND LEMON JUICE

The British Pharmacopœia gives the characters of lemon-juice as follows: specific gravity, 1·030 to 1·040; citric acid, 7 to 9 per cent. w/v. The total solids should not yield more than 3 per cent. of ash. The Board of Trade specify an acidity equal to 30 grains per ounce of citric acid, and a specific gravity (without spirit) not less than 1·030.

Raw lime-juice contains from 3·5 to 8 per cent. of free citric acid. Lime-juice cordial is lime-juice sweetened for use with sugar, which is always found as invert sugar. The citric acid even in the cold comparatively quickly inverts the cane-sugar used. A preservative is frequently added.

According to the *Lancet*, lime and lemon juice have the following composition:

	The Juice of the Lemon.	*The Juice of the Lime.*
	Per Cent.	Per Cent.
Total solid matters	8·80	8·64
Sugar	2·30	0·70
Citric acid	4·57	5·60
Mineral matter	0·35	0·35
Potash	0·15	0·12
Phosphoric acid (soluble) ..	0·010	0·065

The average amount of juice expressed from a lemon was 37·50 per cent. of its weight, while the lime gave 59 per cent.

Fictitious lemon-juice is made by flavouring citric or tartaric acid or citrate of potassium with essence of lemon, and the use of a coal-tar dye has been recorded. When brandy is not used for preservative purposes salicylic acid, sulphites, and boron compounds are employed. Thresh gives from 4 to 8 grains per pint as the quantity of salicylic acid employed in lime-juice cordial. Bunge argues that artificial lemonade should be discarded, as that from boiled fruits contains colloids which modify the irritating action of the acid and salt solution on the membranes.

Tartaric Acid is detected by neutralising some of the sample with caustic soda, and then adding calcium chloride solution, when a white crystalline precipitate of calcium tartrate falls, which formation is accelerated by scratching the sides of the test-tube and by vigorous shaking. Calcium tartrate is soluble in cold caustic potash, while calcium citrate is practically insoluble in the alkali. Further, with citric acid no precipitate is formed with calcium chloride in the cold until after standing some hours.

Free Citric Acid is estimated by titrating 20 c.c. of the sample with $\frac{N}{2}$ NaHO, using phenolphthalein as indicator. Each cubic centimetre of seminormal soda solution equals 0·035 of hydrous citric acid ($H_3C_6H_5O_7H_2O$).

Citric and other Combined Acids are determined as follows: The neutralised juice from the above is evaporated to dryness, and the residue is ignited at as low as possible a temperature. The ignited mass is thoroughly extracted with water, a known volume of standard H_2SO_4 added, and the liquid is boiled and filtered. The filtrate is titrated with standard NaHO, using methyl orange as indicator. The amount of sulphuric acid neutralised 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 neutralised = 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*. Subtracting the free citric acid from the total will give the *combined acid* as *citric*.

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. Two hundred c.c. of the sample are placed in a flask and acidulated with 1 c.c. of phosphoric acid. The flask is connected on one side with a can for steam production and on the other with a

condenser. The sample is submitted to vigorous steam distillation and the condensed liquid collected in a receiver containing distilled water and a few drops of bromine. The tip of the condenser should dip below the surface of the liquid in the receiver to avoid loss of sulphurous acid. The distillation is continued till 400 c.c. of liquid have come over, when the liquid in the receiver is evaporated to 50 c.c. to remove excess of bromine and to concentrate it, acidulated with hydrochloric acid and precipitated with barium chloride. The liquid is allowed to stand overnight and filtered off next morning. The weight of the barium sulphate obtained multiplied by 0·275 gives the amount of SO_2 present in the amount of sample used.

A blank experiment should be made to ascertain what, if any, sulphite or sulphate is obtained from the materials or apparatus.

Sulphites are sometimes directly titrated with standard iodine solution, especially in white wine and beer, but the process tends to give results below the truth. In the process given above, steam distillation is necessary, as in direct distillation there is nearly always some loss of SO_2 owing to its oxidation to SO_3 which is, of course, not carried over in the distillate.

When no glycerin is added, lime-juice cordial in Western Australia (1913) may contain not more than 3 grains of SO_2 per pint.

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 dealt with by the usual methods.

BEER

Beer as brewed at present is a fermented saccharine infusion to which has been added a wholesome bitter. Malt substitutes, such as malted maize, rice, glucose, and invert sugar technically known as 'saccharum,' are largely used. 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 origin of the fermentable materials employed is disregarded by the Excise authorities.

The substitution of bitters other than that of the hop is no offence under the Food and Drugs Acts unless injury to health can follow their use. They are, however, only used in a few—principally small—breweries, and the Inland Revenue publish a list of such places. 'Finings' are used for the purpose of clarification, and almost universally contain isinglass. Gelatin is of no use as a fining agent, and during the preparation of finings the temperature is kept low to prevent its formation. 'Heading powders,' composed of preparations of quillaia cortex and flavouring essences, and saccharin, are prohibited by the Revenue.

Two methods of fermentation are in use, the 'High' and 'Low.' The 'high,' or 'surface,' fermentation as used in England takes place at a higher temperature and is of shorter duration than the 'low' 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.

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, coloured and flavoured with roasted malt, which gives it the black colour.

4. Stout, a stronger variety of porter.

5. Lager or German beers contain more extractive and less alcohol than English brewed beers. These beers are very liable to secondary fermentation unless kept at a very low temperature.

A beverage is classed as non-alcoholic if it contains less than 2 per cent. of proof spirit. Such beverages, if kept for some time, ferment, the spirit increasing to 3, 4, or 5 per cent. proof spirit.

Analysis of Beer.

The large amount of gas present, which causes the beer to froth during pipetting, measuring, and distilling, must be got rid of before starting the analysis. This may be done in a 'beer-beater' or by 'tossing.' In the latter process the beer is quickly poured from one vessel to another and back again several times, or it may be run through a quick filtering paper. These processes occasion no loss of alcohol.

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

Direct Distillation.—A hundred c.c. of the sample are distilled until about 90 c.c. 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 c.c. mark with distilled water, mixed, and the specific gravity taken with a bottle. The amount of alcohol is found by means of the alcohol tables.

Tabarie's Indirect Method.—The specific gravity of the original liquid is first accurately determined. A measured quantity, say 100 c.c., is then boiled until all the alcohol and other volatile matters are evaporated. This will generally be the case if the liquid is boiled down to one-third of its original bulk (a spirit requires to be taken nearly to dryness.) The residue is then cooled, made up to its original bulk with water, and the specific gravity taken at 15·5° C., when

$$\frac{\text{Sp. gr. of the original liquid}}{\text{Sp. gr. of the 'extract'}} = \left\{\begin{array}{l}\text{Sp. gr. of alcohol evapo-}\\ \text{rated.}\end{array}\right.$$

A more accurate method is to subtract the present gravity (*i.e.*, the gravity of the untreated sample) from the extract gravity (*i.e.*, the gravity of the de-alcoholised beer), and subtract the result from 1,000, when the result gives the gravity of the alcohol evaporated. To give an example: A beer has a gravity of 1034·3, while the extract has a gravity of

1044·7. The former subtracted from the latter gives 10·4, and this subtracted from 1,000 gives 989·6, and on looking up a gravity of 0·9896 in the tables it is seen that this represents 7·50 per cent. of alcohol by volume.

The tables in present use are Thorpe's 'Alcoholometric Tables' (Longmans, Green and Co.).

The Extract.—The extract is estimated from the de-alcoholised 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' or 'apparent solids' contained in 100 c.c. of the sample. From this is subtracted the figure obtained by multiplying the ash by 2·07, and the original ash added; for ordinary working it is near enough to simply subtract the ash from the 'apparent solids.' This correction for ash is based on the assumption that a 1 per cent. solution of mineral matter from sugar is 1008.

Ash.—The ash is obtained by igniting the extract, obtained by evaporating a portion of the beer, at a low temperature.

Sodium Chloride.—As determined by exhausting the ash with water, and estimating the chlorides with $\frac{N}{10}$ $AgNO_3$, using neutral potassium chromate as indicator, the result tends to be below the truth. Each cubic centimetre of $\frac{N}{10}$ $AgNO_3$ = 0·00585 NaCl or 0·00355 chlorine. Salt is 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 'fixed' acidity 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 c.c. of the beer are diluted to 100 c.c., and evaporated to dryness. This is again diluted, titrated with $\frac{N}{10}$ sodium hydrate, using litmus

as indicator. The number of cubic centimetres used multiplied by 0·009 = fixed acid as lactic.

Volatile Acid.—Twenty c.c. of the original sample are well diluted with water, and titrated with $\frac{N}{10}$ NaHO, using litmus as before. The number of cubic centimetres of alkali used *minus* the number of cubic centimetres of NaHO required for the fixed acid, multiplied by 0·006, will give the amount of volatile acid as acetic.

Fresh worts contain practically no volatile acid and the amount produced during fermentation and storage 'is negligibly small' so long as the beer remains sound (Thorpe and Brown).

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* (picrotoxin), nux vomica (strychnine), and picric acid, have been used, but their recurrence is unlikely.

One thousand c.c. of the sample are evaporated to one-half and neutral lead acetate added; 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 c.c. 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. If the filtrate 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 sulphuric 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.—Salicylic and boric acids are seldom used.

When hops are being dried in the kiln, sulphur (half a pound per 10 bushels of green hops) is burnt beneath them during the first two or three hours of drying. This bleaches the hops, and the part of the sulphur retained makes them more attractive, changes the odour, prevents fermentation, and, by causing the petals to open, hastens the drying process. The hops contain about 0·25 per cent. of SO_2. This sulphurous acid passes off during the boiling of the wort, to a large extent at any rate. Some, however, seems to be retained, as Bonn found beer free from added sulphurous acid to contain 0·0128 to 0·0256 gramme sulphurous acid per litre. J. L. Baker (*Journ. Inst. Brewing*, 1911, p. 466) says that sulphur dioxide combines with the aldehydes, ketones, sugars, and alcohol.

However, sulphites, usually in the form of bisulphites of lime, are frequently added to beer as a preservative.

Detection of Saccharin.—C. Schmitt recommends that 100 c.c. should be acidulated with sulphuric acid, and shaken with 50 c.c. 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, saccharin 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. During fermentation the specific gravity of the wort is diminished, the weight of alcohol being approximately half that of the saccharine matters destroyed.

The Original Gravity Table now in use is that of Thorpe and Brown. It will be found in *Journ. Inst. Brewing*, 1914, p. 569, and in *Analyst*, 1915, p. 122. An extended table interpolated to one-hundredths of a degree has been prepared by G. C. Jones and J. L. Baker entitled 'Original Gravity Tables' (London: *Brewers' Journal*, 2s. 6d. net). Thorpe and Brown's Table was attached to and given force of law by the Finance Act, 1914 (Session 2).

The alcohol is first estimated by distillation. The specific gravity of the distillate is deducted from 1,000; the difference is the *spirit indication*. From the original gravity table the number of degrees of 'gravity lost' are found; thus, suppose the spirit indication is 11·5, taking 11 in the first column, and under 0·5 in the seventh column yields 52·35 equal to 'gravity lost.'

This figure is added to the specific gravity of the de-alcoholised 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)	28·2
Specific gravity of de-alcoholised beer	1014·2
Original gravity of wort =	1042·4

Arsenic.—Arsenic may occur in beer owing to the use of arsenical fuel in the drying of the malt and hops, or through the use of sugars prepared with arsenical sulphuric acid. The Royal Commission on Arsenical Poisoning, 1903, laid down as a limit for beer, etc., $\frac{1}{100}$ grain of As_2O_3 per gallon. See Chapter on 'Poisonous Metals.'

Analysis of Some Typical Beers.

	Specific Gravity at 15·5° C.	*Alcohol (% by Weight).*	*Extract.*	*Ash.*	*Acidity as Acetic.*	*Proteins.*
Bitter Ale	—	5·4	5·4	—	0·1	0·16
Burton, Mild ..	—	5·4	5·1	—	0·1	0·21
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	—	—	—
Allsopp's Pale ..	1·0144	6·4	4·4	—	0·3	—
Friary Invalid Stout	—	5·4	7·1	0·4	0·2	0·58
Stout, Guinness XX.	1·0244	5·0	5·5	—	0·2	—
Porter, Barclay ..	—	5·4	6·0	0·4	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

In the preparation of wine the grapes are generally separated from the stalks, placed in a press, and the juice expressed. In many instances the grapes

are simply trodden. This especially applies to red grapes, as, when making claret, mechanical pressure would extract an excess of tannin and colouring matter. The juice, or 'must,' is then placed in vats for fermentation. The addition of yeast is unnecessary, as the requisite organisms exist naturally on the skins of the grape. The juice before fermentation contains about 20 per cent. of solid matter; from 12 to 18 per cent. is glucose, the remainder containing albuminous matters, potassium-hydrogen tartrate, calcium tartrate, traces of gum, colouring matter, mineral matter, etc. During 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 tartrate, and run off into casks, in which an after-fermentation takes place, resulting in a further deposit of tartrates, etc. The wine is then drawn off into fresh casks, in which it is kept for various periods to clear, 'age,' or 'mature.'

The 'dry' wines, such as Burgundy, Rhine, Moselle, and Gironde, contain no sugar and a comparatively large amount of acid. The 'sweet' wines, as port and Madeira, contain a considerable amount of undecomposed sugar. As a rule, red wines are much less acid than white wines. It is only when they are sugar-free that they appear acid to the palate, but chemically they contain less than white and sweet wines.

The proportion of sugar and acid best adapted for the production of wine is 40 to 1. If the acid is in excess, the 'must' is diluted and the necessary amount of glucose or cane-sugar added. 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 prevents unfermented sugar undergoing subsequent fermentation. The proportion of alcohol in 'fortified' wines is sometimes as high as 22 per cent., but in natural wines it rarely exceeds 13 per cent. By the English Customs regulations 10 per cent. of brandy is allowed to be added to wines in bond.

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 to 0·5; glycerin from 1·3 to 0·6; phosphoric acid from 0·06 to 0·02 per cent. The commercial value is 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.

Under Anglo-Portuguese Commercial Treaty Acts, (*Board of Trade Journal*, September 28, 1916), the description 'Port' or 'Madeira' is deemed to be a false trade description within the meaning of section 3 of the Merchandise Marks Act, 1887, when applied to: (1) Wine or other liquor, other than wine the produce of Portugal and the Island of Madeira respectively. (2) Wine the produce of Portugal, in respect of which a certificate issued by the competent Portuguese authorities to the effect that it is a wine to which by the law of Portugal the description 'Port' may be applied, has not been furnished. The *Lancet* appointed an Analytical Commission on Port Wine and the Vineyards of the Alto Douro (*Lancet*, 1907, ii., 1705).

Sherry is defined as the fermented expressed juice of the grape, the produce of Jerez (Xerez) de la Frontera, and shipped from Cadiz.

The 'plastering' of wines consists in adding calcium sulphate (plaster of Paris, gypsum) to the 'must' or the wine. This is claimed to add to the keeping properties of the wine by removing any excessive acidity. Calcium tartrate and potassium sulphate are formed. The calcium salt, being insoluble, is deposited with the 'lees,' while the potassium sulphate remains in solution. Both France and Spain prohibit the addition of sulphate of lime to wines whenever it results in the liquid containing more than 2 grammes of potassium sulphate per litre. Generous, dry, and vigorous wines (sherry, Malaga) are excepted and may have sulphate of lime added to the degree necessary for their good preservation. Moderate plastering is absolutely essential in sherry-making, unplastered sherry having a filthy

taste. The calcium sulphate is added to the extent of 2½ pounds to 1 ton of grapes. The addition stimulates the formation of ethers, and the amount of potassium sulphate seldom exceeds 0·33 per cent. The ash of pure wine does not exceed 0·35 per cent., but in samples of sherry it may reach 0·5 per cent., and is composed almost entirely of sulphates.

Many 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; mixing supplies the trade with a uniform product. The Board of Customs and Excise control at place of manufacture the mixing of foreign and British wines and altogether prohibit retailers blending; not more than 15 per cent. of foreign wine may be blended with British wine.

Analyses of Typical Wines.

	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 ..	0·9950	12·0	2·4	0·2	0·22	0·05	0·42	0·17	0·18
White French	0·9920	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 ..	0·9934	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 ..	0·9940	17·2	4·2	2·5	0·40	0·02	0·27	0·15	0·18
Port	1·1004	18·5	7·5	4·3	0·30	0·05	0·31	0·08	0·22
Madeira ..	0·9939	16·7	5·0	2·1	0·40	0·04	0·54	—	—
Marsala ..	0·9966	17·5	5·4	3·2	0·20	0·02	0·32	—	—
Greek	0·9931	13·9	2·5	0·4	0·40	0·04	0·23	0·18	0·30
Hungarian ..	0·9921	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	—

The Paris Municipal Laboratory adopt the following standards: 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.

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

The following are some of the conclusions of a German Government commission:

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

(*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 c.c.

'Pasteurisation' is largely resorted to in France to effect artificial ageing, and to ensure keeping. 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 or other diseases of bacterial ætiology are restored by this treatment, owing to the destruction of the disease organisms.

When wine is left in an atmosphere of nitrogen, fermentation stops, the organisms die, rapidly settle to the bottom, and the wine takes on the clear limpid appearance associated with age. It seems probable that this is the change normally taking place, only

the absorption of the atmospheric oxygen from the air left in the bottle is much more gradual.

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

The greater part of fictitious wine is made from dried raisins imported from Spain and the Levant. F. Schaffer has published the following analyses of these:

	A.	*B.*	*C.*
	Per Cent.	Per Cent.	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,' sold in the temperance interest and for sacramental purposes, generally consist of clarified fruit-juices preserved with salicylic and boric acids, often with the addition of saccharin.

The Analysis of Wines.

Specific Gravity is taken at 15·5° C.

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

Extract.—This is estimated by drying 5 grammes. A very close approximation can be obtained as follows: From the specific gravity of the de-alcoholised liquid is subtracted 1000; the remainder, divided by 4·6, will give the number of grammes of extract per 100 c.c. In the case of very sweet wines, it is better to use

the 3·86 divisor and correction for ash as described under 'Beer.' 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 determining the reducing power of the liquid on Fehling's solution. One hundred c.c. of light wine, or 50 c.c. of sweet wine, treated as above and diluted to 200 c.c., 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 'Self-raising Flour.'

Acidity—*Fixed Acid.*—This is determined by diluting 20 c.c. 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 phenolphthalein as indicator. The number of cubic centimetres of soda used multiplied by 0·0075 = *fixed acid as tartaric.*

Volatile Acid.—Twenty c.c. of the original wine is well diluted with water, and titrated with $\frac{N}{10}$ NaHO, using phenolphthalein as before. The number of cubic centimetres of alkali used in the case of the fixed acid is deducted from the result. The remainder multiplied by 0·006 = *volatile acid as acetic.*

Free Tartaric Acid and Potassium Bitartrate.—In the presence of a small amount of other free acids the detection of a considerable amount of free tartaric acid affords strong evidence that the wine is artificial. Nessler recommends the following qualitative test: Twenty c.c. 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 are 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 c.c. each) are introduced into two flasks, a few drops of 20 per cent. solution of potassium acetate being added to the second flask; 200 c.c. 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° and 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 assists in the separation of the precipitates.

Detection of Foreign Colouring Matter.—Dupré's method: A 10 per cent. solution of the best transparent gelatin is prepared, and 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 wine. After twenty-four hours the cubes are removed, washed with a little cold water, then cut in half. 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 *fuchsin, cochineal, logwood, litmus, beetroot, Brazil-wood, indigo*, etc., penetrate 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 blue.

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.

The Paris Municipal Laboratory use the following test: A few drops of the wine are dropped on to a piece of recently calcined lime. *Natural red wine* gives a yellowish-brown coloration; wine coloured with *fuchsin* or *Brazil-wood* gives a rose colour; wine coloured with *logwood* gives a reddish-violet colour. Other Paris tests will be found in the *Analyst*, 1885, pp. 181 and 196.

Logwood may be detected as follows: Twenty c.c. of the sample are well shaken with about 2 grammes of finely powdered manganese dioxide, and the filtered liquid treated with zinc and hydrochloric acid, which destroys the brown coloration of the oxidised logwood. The colourless and neutralised 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.

Rosanilin salts (*fuchsin* and *magenta*) may be detected, according to A. H. Allen, by rendering 50 c.c. 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 c.c. of water and the same measure of alcohol are added, and the liquid is shaken with 10 c.c. 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 rosanilin 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 *anilin colours* in wines, fruit-juices, etc., Curtman has published a test, dependent upon Hofmann's isonitril reaction: To 4 c.c. of the wine are added 4 c.c. 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 rosanilin* 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 *anilin blue, purple, violet, magenta, red,* and many *yellow* and *green anilin colours.* This test is now used in the U.S.P., where normal potash solution is specified.

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 Curtman test: To 4 c.c. of the wine (or beer) add 2 c.c. of methyl alcohol and 2 c.c. 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.—The processes given under 'Milk' can be used for its detection. Boric acid is stated by many authorities to be a normal constituent of wine.

Sulphites.—Detected and estimated as given under 'Lime-Juice.' In white wines. the total sulphur dioxide may be estimated by the U.S. Dept. of Agric. process: To 25 grammes of the sample are added 25 c.c. of normal potassium hydroxide. After gently shaking a few times, the solution, after an interval of fifteen minutes, is mixed with 10 c.c. of dilute sulphuric acid (1:3), and then titrated with $N/50$-iodine with starch as indicator.

Saccharin (*Benzoyl sulphonic-imide*) is detected by Schmitt's process as given under 'Beer.'

CIDER

Cider is the expressed juice of the apple that may or may not have undergone alcoholic fermentation. The first column of figures given below shows the range of five *Lancet* analyses of English

bottled ciders, the second column figures given by G. Filandeau (*Y.B.P.*, 1912) as typical of carefully stored French ciders of good quality, in percentages:

Sugar	0·71 to 6·25	—
Alcohol per cent. by volume	5·00 „ 9·86	3·9 to 5·1
Extractives	1·89 „ 8·22	2·26 „ 5·32
Mineral matter	0·25 „ 0·35	0·25 „ 0·29
Volatile acidity as acetic acid	0·10 „ 0·34	0·19 „ 0·24
Fixed acidity as malic acid ..	0·21 „ 0·41	0·39 „ 0·50
SO_2 per litre	—	0·016 „ 0·033

Aerated, flavoured sugar solutions quite free from apple-juice are sometimes sold as cider, such sale being an offence under the Merchandise Marks Act. They sometimes contain tartaric acid, which we believe is not present in apple-juice.

Especially when the liquor is brewed from unsound apples, from apples not cleaned from earthy material, or irresponsible fermentation has been allowed, preservatives are added. Sulphites, benzoates, salicylates, and borates are used.

SPIRITS

Various materials, such as wheat, maize, barley, fruit-juices, etc., yield alcoholic liquids on fermentation. When the alcoholic liquid so obtained is distilled, the distillate constitutes a 'spirit.'

Brandy.—The Royal Commission concluded that the term 'brandy' is applicable to a potable spirit manufactured from fermented grape-juice and from no other source.

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

Whisky.—Whisky is prepared from grain, mostly barley, both malted and raw. The smoky flavour

is due to malt 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.

The Royal Commission on Whisky and Potable Spirits decided the name 'whisky' could be applied to describe any potable spirit obtained by distillation from a mash of cereal grains saccharified by the diastase of malt. The term, therefore, extends to the products of stills other than pot-stills.

Rum.—Rum is obtained by the distillation of the fermented juice of the sugar-cane or molasses. It is coloured by caramel or from the wood of the cask in which it is stored, and flavoured by means of sugar-cane leaves or pure fruit. The flavouring substances are placed in the still along with the mash or megass and not added to the liquor after distillation. The characteristic odour of rum is due to ethyl butyrate. The specific gravity ranges from 0·874 to 0·926; alcohol from 50 to 70 per cent.; total solids from 0·7 to 1·5 per cent.

Manufacturers of artificial rum have given earnest consideration to the composition of the genuine article and many of their sophistications will be found normal in the content of aldehydes, acids, esters, higher alcohols, and furfural. An abnormally high dosage with ethyl butyrate sometimes reveals the fraud. The highest ester figure found by Sanarens in genuine rum was 938 grammes per 100 litres of absolute alcohol present.

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, made from rye.

Analysis of Spirits.

The most frequent form of adulteration of spirits is the addition of water. Notices to the effect that no definite percentage of grape spirit is guaranteed are very frequent in public-houses. These protect the vendor from possible action under the Food and Drugs Acts, and are often so worded that the real significance is lost on the uneducated person. The alcoholic strength should be determined. Methyl and amyl alcohols should be tested for. Caramel is detected by its bitter taste and the reducing power it exerts on Fehling's solution.

In estimating the various 'impuretés' a certain amount of practice is necessary to ensure concordant results. The following estimations are of value: The ethers, aldehydes, furfurals, higher alcohols, free and fixed acidity, and the amount and character of the solids left on evaporation. The methods are described in 'Analysis of Potable Spirits,' by S. A. Vasey (Baillière, Tindall and Cox).

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. Even then the liquid in the distillation flask requires to be taken as near to dryness as is possible without burning the residue to get all the alcohol off.

With whisky, brandy, and unsweetened gin, the specific gravity of the sample referred to alcohol tables will give an alcohol content not much below the truth. The difference between the alcohol thus roughly determined and the real content is called 'the obscuration.'

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). See Appendix for Central Control Board (Liquor Traffic) modifications.

Ethers.—The ethers present in genuine brandy are considered to consist mainly of acetic ether, and usually amount to about 100 parts per 100,000, *calculated on the actual amount* of alcohol present. This device of calculating on the *actual alcohol* present enables us to compare brandies that may vary in their alcoholic contents. It is generally adopted for all the other constituents of potable spirits.

Take 100 c.c. of the sample, measured at 15·5° C., and distil slowly down to about 20 c.c. Remove the flame, and allow the distilling flask to cool. (A good condenser is a necessity, a glass worm being suitable.)

Now add 20 c.c. of water to the contents of the flask, and distil until 100 c.c. of distillate have been obtained. Take the specific gravity of this liquid at 15·5° C., without wasting any of it—*i.e.*, if a specific-gravity bottle is used, dry it first, and do not use the distillate to rinse it out with. After taking the specific gravity, calculate the alcohol. Pour the distillate into a 300 c.c. flask. Add a drop of phenolphthalein solution, and neutralise any free acid that may have come over with the alcohol. The quantity is of no consequence, as it does not represent the whole of the free acid in the sample. Having neutralised *exactly*, add 25 c.c. of decinormal alcoholic soda to the contents of the flask, and saponify under a reflux condenser for two hours.

After the saponification is complete, cool, and titrate back the excess of soda with $\frac{N}{10}$ sulphuric or hydrochloric acid. Each c.c. of soda used in saponifying the ethers corresponds to 0·0088 gramme of ethyl acetate.

It is important to purify the corks used by soaking in successive quantities of alcohol for two or three days beforehand.

The following example will serve as an illustration:

One hundred c.c. of distillate from a brandy of known purity was neutralised by 2 c.c. of $\frac{N}{10}$ alcoholic soda, and 25 c.c. of the $\frac{N}{10}$ soda was added, and 25 c.c. placed in another flask to serve as a 'blank.' After both had been refluxed for two hours, they were titrated with $\frac{N}{10}$ acid. The blank required 24·5 c.c., and the sample 18 c.c., the difference being 6·5 c.c.;

this, multiplied by the factor 0·0088, gives 0·0573, and the sample contained 50 per cent. of absolute alcohol by volume, so that the ethers present amounted to 114·6 parts per 100,000 of absolute alcohol by volume.

There is no method of distinguishing between the ethers natural to brandy and any specially prepared and added to stultify the analysis. It would, however, be difficult to so adjust the amount of other constituents as to obtain a satisfactory flavour and bouquet.

Aldehydes.—Five or ten c.c. of distillate* are diluted so as to contain 50 per cent. of absolute alcohol by volume. The liquid is placed in a cylinder, 4 c.c. of bisulphite fuchsin reagent added, and the whole made up with 50 per cent. spirit to 20 c.c. Five c.c. of the standard aldehyde are treated in the same way, and the mixtures allowed to stand twenty minutes, when they are compared.

The standard solution of aldehyde is made by dissolving 1·386 grammes of ammonia aldehyde in 50 c.c. of 96 per cent. alcohol. To this is added 22·7 c.c. of normal alcoholic solution of sulphuric acid. This throws out ammonium sulphate. The volume is made up to 100·8 c.c., allowed to stand twenty-four hours, and filtered. It then contains 1 gramme of aldehyde per 100 c.c. solution. This is diluted

* To obtain material for use in determining aldehydes, furfural, and higher alcohols, it is convenient to distil 50 or 100 c.c. of the sample, and to adjust the strength to about 50 per cent. of absolute alcohol. If employed at a greater or less strength the colours obtained on comparison with the standard solutions will not be so satisfactory.

It is necessary to use pure alcohol for the preparation of standards, etc. Rectified spirit free from aldehydes, furfural, and higher alcohols, can usually be obtained. If not, distillation over potash or soda will give a distillate free from esters. To get alcohol free from aldehydes, including furfural, a litre is dosed with 3 or 4 grammes of meta-phenylene-diamine hydrochloride and left to digest for several days, when the alcohol is slowly distilled, the first few c.c. being rejected and the distillation stopped when nine-tenths of the alcohol has been distilled (Girard and Cuniasse). The prolonged digestion at room temperature may be replaced by an hour's boil under a reflux condenser.

for use to a strength of 0·05 or 0·1 gramme of aldehyde per litre.

The bisulphite solution is made to a specific gravity of 1·360.

To make the reagent, take 150 c.c. of the 0·1 per cent. solution of fuchsin, 100 c.c. of the bisulphite of soda, add them to 1 litre of water, and to this mixture add 15 c.c., of pure 66 per cent. sulphuric acid. The mixture is shaken, and should be quite clear and colourless after some hours.

The solutions of fuchsin and bisulphite of soda should be kept separately in the dark, and mixed when required. When mixed, the solution should not be kept for more than one month.

Furfural.—Take 10 c.c. of distillate diluted to 50 per cent. of alcohol, and place in a graduated tube.

Ten c.c. of standard furfural (0·005 gramme per litre) is placed in a similar tube. To each add 10 drops of pure anilin oil (which should be colourless) and 1 c.c. of acetic acid (pure and free from furfural). After fifteen minutes compare the tints.

Furfural characterises pot-still spirit, and is absent from patent-still spirit.

Higher Alcohols—Vasey's Modification of Saville's Test.—Take 10 c.c. of distillate, adjusted to 50 per cent. strength. To this is added 10 c.c. of monohydrated sulphuric acid, specific gravity 1·794 (made by adding 18 c.c. of water to 100 c.c. of sulphuric acid, 1·84 specific gravity), in a clean test-tube (1 inch by 6 inches). The mixing must be thorough, and considerable heat is generated. A small piece of quill tubing is then dropped into the tube (to prevent bumping), and the contents are boiled over a naked flame, and a note of the time made. As soon as a few bubbles of steam rise from the fragment of glass tubing, the tube is withdrawn from the flame for twenty seconds, and then returned, and so on. This is carried on for five minutes, when it is cooled under the tap. The solution is then placed in a graduated cylinder.

A standard solution is made thus: 10 c.c. of a standard solution* of iso-butylic acid alcohol in 50

* Two grammes of iso-butylic alcohol are dissolved in a litre of 50 per cent. alcohol.

per cent. alcohol is placed in the same test-tube that was previously employed, and treated with 10 c.c. of the same sulphuric acid (1·794) for exactly the same time. The colours are then compared, and the amount of higher alcohols, as iso-butylic alcohol, is calculated. By multiplying by 1·19 the result may be expressed in terms of amylic alcohol.

Estimation of Acidity, Volatile and Fixed.—For the estimation of the fixed acidity the residue after distillation may be employed. It should be washed out into a dish, and evaporated two or three times with addition of distilled water, and titrated with $\frac{N}{10}$ baryta and phenolphthalein.

To estimate the volatile acidity: 100 c.c. of the original brandy are titrated with baryta. The number of cubic centimetres of decinormal alkali required for neutralisation of the fixed acidity subtracted from the number required for the total acidity gives the volatile acidity, which may be calculated to acetic acid (1 c.c. of alkali = 0·006 gramme acetic acid). The fixed acidity is calculated to tartaric acid (1 c.c. of $\frac{N}{10}$ alkali = 0·0075 gramme of tartaric acid), though it is probably in part tannic acid.

Methyl Alcohol is detected by the Riche and Bardy test: Mix together in a flask 10 c.c. of the sample, 15 grammes of iodine, and 2 grammes of amorphous phosphorus, and distil off the methyl and ethyl iodides formed into 30 c.c. of water. Separate the heavy oily drops from the water, and mix with 5 c.c. of anilin 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 c.c. 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 c.c. 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 anilin violet), which is deeper according as the percentage of methyl increases. The presence of the anilin 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 methyl alcohol, the wool takes on the violet colour, the depth of tint giving a fair approximate indication of the proportion present. The skein of wool is then compared with a standard set of skeins made from mixtures containing known percentages of methyl alcohol.

C. Simmonds has elaborated Denigès' process for the determination of small quantities of methyl alcohol and G. C. Jones has further stabilised it (*Analyst*, 1912, p. 16; 1915, p. 218).

Fusel Oil (*Amyl Alcohol*) is best detected as follows: About 100 c.c. of the spirit are very slowly distilled at as low as possible a 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 (*amyl acetate*) is evolved.

The Marquardt-Allen process for the estimation of fusel oil 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.

One hundred and fifty c.c. of the sample are diluted with water to a specific gravity of about 0·980, and agitated with 50 c.c. of pure chloroform for a quarter of an hour. The aqueous layer is separated and shaken with another 50 c.c. of chloroform, and subsequently treated a third time. The 150 c.c. 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 c.c. 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 c.c. have passed over, when 80 c.c. of water is added to the residue, and the distillation continued till only 5 c.c. 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 c.c. 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 c.c.; 50 c.c. 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 c.c. 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 c.c. 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 as such. Very old brandy contains considerable quantities of amylic alcohol,

some of which, however, is probably present in the form of an amylic or butylic ether.

Interpretation of Results.—In well-matured brandy 'impuretés' are small in amount. The ethers vary from a little under 80 parts per 100,000 to over 200 per 100,000.* The higher alcohols appear to vary from about 100 parts up to over 250, or even 300, per 100,000. The aldehydes are considerably less, being from about 10 parts to over 40, and the furfural from under 1 part to over 3 parts per 100,000. It appears that the amount of ethers increases on keeping. If made from 'sick' wines, the unpleasant odour of the first portion of the distillate is such that it has to be discarded, and as the ethers are largely contained in the first fraction, brandy so prepared will probably be low in ethers.

It was formerly supposed that amyl alcohol was an important factor in producing the evil effects of unmatured spirits. No definite proof of this has been given, while A. H. Allen, who took every evening for some weeks a teaspoonful of fusel oil, showed that so far as he personally was concerned this had very little effect.

The relatively small amount of furfural in old brandy should be remarked. It is the most poisonous constituent present in spirits, and the fact that brandy contains only a small amount may mean that more of this spirit can be tolerated.

The sum total of the free acid, aldehyde, furfural, ethers, and higher alcohols, gives the total secondary products or 'the coefficient of impurities.' The *Lancet* Commission showed that for special fine brandies this coefficient varies from 300 to 646, but may fall to 250 parts per 100,000 of absolute alcohol present for inferior but genuine brandy. Grain and beet spirits are comparatively free from secondary products, furfural especially being absent. Gin is also low in total secondary products. Jamaica rum is very high in ethers (amounting to over 400 grammes of ethyl acetate per 100 litres of absolute alcohol

* These figures are, of course, in terms of parts per 100,000 of absolute alcohol.

present), and contains more acids and furfural than brandy. Whisky closely resembles brandy, but the furfural is high.

SAUSAGES

Sausages consist of a mixture of finely minced meat and bread or meal, with the addition of salt, pepper, spices, and herbs. They are sometimes coloured with a coal-tar dye or oxide of iron. Saltpetre is sometimes used to enhance the colour, and to act as a preservative. Sulphites are often added to hide the fact that tainted meat has been employed. The intestines in which the meat is packed come from abroad preserved with salt, and they have been known to contain mineral poisons. The meat used is sometimes not above suspicion, the carcasses of very emaciated cattle, known as 'mincers,' being used for the purpose. Horse-flesh may also be used. Sausages soon decompose, and most wholesale manufacturers use some preservative, generally boric acid. The quantity is generally about 20 grains per pound. Out of 32 samples we examined, 22 contained boric acid in amounts varying from 4·1 to 71·6 grains per pound of boric acid. This preservative appears to preserve the meat rather than the bread. Whereas a sausage without the addition of boric acid will generally smell offensively before moulds appear, such smell is not generally perceptible before the appearance of moulds in sausages containing it.

Decomposition is best detected by boiling the sausage with water and adding freshly prepared lime-water, when an offensive odour will be perceived.

Horse-flesh may be detected by the presence of glycogen. About 200 grammes are boiled with an equal quantity of water for an hour. When cold, 10 c.c. of strong nitric acid are added. The infusion is filtered. To the filtrate is added freshly prepared hot iodine solution, so that the two liquids do not mix (iodine 1 gramme, potassium iodide 2 grammes, water 100 c.c.). If horse-flesh be present a reddish-violet zone appears at the junction of the two fluids.

The presence of glycogen is not positive evidence of horse-meat, as it occurs in meat extracts, young veal, and in the livers of cattle. Dextrin from the starchy substances added to sausages will also give the reaction. Robertson recommends the addition of acetic acid during the boiling process, and the employment of a 10 per cent. solution of iodine in potassium iodide. Although the glycogen in horse-flesh exists in comparatively large quantity, and does not rapidly disappear, it is liable to undergo decomposition with age, and if the horse-flesh be smoked, the glycogen will be destroyed.

By precipitin reactions it is possible to detect not only horse-flesh, but that of any other animal and other native proteins. The preparation of the various anti-sera takes a long while, say six weeks; so that, unless a peculiar flesh is anticipated, or a stock anti-serum is available, the test is not in the domain of practical analysis.

Boric Acid may be conveniently estimated by the following process: Twenty grammes of the meat are mashed with 2 c.c. of 50 per cent. caustic soda solution in a platinum dish, and then heated over a flame till the mass is charred throughout. The carbonised mass is extracted with hot distilled water, the total amount used being under 100 c.c. and the various lots of wash-water used being passed through a filter-paper. The filter and contents are put back in the dish and ignited till white. The ash is taken up with dilute hydrochloric acid, and added cautiously to the alkaline extract. The mixture is made acid to litmus-paper and about 2 c.c. of 50 per cent. calcium chloride solution are added. A drop of phenolphthalein solution is added, and the liquid is transferred to a 200 c.c. flask. Caustic soda solution is added till alkaline to remove unnecessary lime from solution, and the bulk is made up to the mark with distilled water. After shaking, the liquid is filtered, and 100 c.c. (=10 grammes of sausage) is treated with normal sulphuric acid till neutral to methyl orange. The liquid is brought to the boil to drive off carbon dioxide, cooled, and half its bulk of neutral glycerin added. It is then titrated with

decinormal alkali, using phenolphthalein as an indicator. Each cubic centimetre of decinormal alkali =0·0062 boric acid.

Starch is estimated by Mayrhofer's method: About 60 grammes of the sausage are heated on the water-bath with approximately 8 per cent. alcoholic potash, when, if the sausage be pure, all except a little cellulose is dissolved. The solution is diluted with warm alcohol to prevent gelatinisation and filtered. The insoluble residue which contains any starch is washed with alcohol till the washings are no longer alkaline, then treated with a weak acetic acid solution and made up to a definite volume. On adding alcohol to an aliquot portion, the starch subsides and is filtered off, washed with alcohol and ether, dried and weighed. Glycogen, if present, will be precipitated with the starch (*Analyst*, 1911, p. 501).

In this country added starch takes the form of stale bread. In Victoria, farinaceous matter, calculated as starch, is limited to 6 per cent.

Sulphites can be detected and estimated by the process given under 'Lime-Juice.' Twenty grammes of sausage-meat mixed with water is a convenient quantity to use. If decomposition has commenced, a flask containing a 1 per cent. solution of copper sulphate should be interposed to wash the steam free from sulphides (Winton and Bailey's modification).

Nitrates.—We find diphenylamine to be the readiest means of detecting nitrates in sausage-meat. Several c.c. of a solution of diphenylamine in concentrated sulphuric acid (for qualitative purposes, the strength matters little—any quantity from 1 milligramme to 1 gramme per 100 c.c. of acid can be used) are poured over a little of the sausage-meat. A blue colour shows the presence of a nitrate.

For the estimation of nitrates, the phenol sulphonic acid method used in water analysis can be applied to an aqueous extract if chlorides are first removed by silver sulphate as in Chamot, Pratt, and Redfield's modification of the process.

THE EXAMINATION OF OILS AND FATS

The analysis of oils and fats requires skill, and the interpretation of the results can only be successfully undertaken by those with special training. 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. Samples of the same oil may vary very much, according to the place of production, method of manufacture, purification, etc.

'Hardened' Oils.—Any oil containing glycerides of unsaturated acids can be converted into a hard fat (or into an oil or fat of any intermediate consistency) by the addition of hydrogen to the molecule. Olein thus becomes stearin. The reaction is induced by a metallic (generally nickel) catalyst. While the acid value, saponification value, and unsaponifiable matter are not appreciably affected, 'hydrogenisation' raises the melting and solidifying points, and lowers the iodine value. It interferes with some otherwise useful tests: Halphen's test for cotton-seed oil and the octobromide test for marine oil. It is said to have no effect on sesamol, and not to interfere with Bomer's phytosterol acetate test, nor with Tortelli and Jaffe's colour test for marine animal oils (*Analyst*, 1915, p. 14).

Detection of a hydrogenised product is usually effected by the finding of the catalyst—*i.e.*, nickel. For this Tschugaeff's dimethylglyoxime is frequently used. The method of application varies; that recommended by Prall is as follows:

One hundred grammes of the oil are ashed in a platinum dish. The ash is dissolved in dilute hydrochloric acid, the solution heated to drive off the greater part of the acid, and then saturated with ammonia. After standing for some hours, the precipitated iron and aluminium hydroxides are filtered off, the filtrate evaporated to dryness, and the residue treated with ammonia and alcoholic dimethylglyoxime solution. 0·01—0·1 mgm. of nickel gives a red coloration. Brunck (*Analyst*, 1914, p. 375)

says that a great excess of ammonia or a high concentration of alcohol slightly increases the solubility of nickel dimethylglyoxime. Some workers precipitate the nickel from a solution slightly acid with acetic acid. R. H. Kerr describes a fugitive red coloration on the addition of dimethylglyoxime and ammonia when testing hydrochloric acid extracts of cotton-seed oil for nickel, but its rapid fading renders it unlikely to mislead.

Atack (*Analyst*, 1913, p. 316) prefers to use Tschugaeff's *a*-benzildioxime, which he finds more sensitive.

'Accessory Substances.'—In ability to promote growth and well-being of the subject, butter-fat and perhaps a few other fatty substances such as cod-liver oil are superior owing to their content of fat-soluble accessory substances ('vitamines'). The latter also occur in oleo-oil margarine, but are entirely absent from lard and from lard-substitutes made from vegetable oils. Halliburton and Drummond (*Journ. Physiology*, 1917, p. 235) have shown coconut oil, cotton-seed oil, and arachis oil to contain little or no fat-soluble accessory substance. These oils are frequent in inferior brands of margarine, and these workers say 'it would be truer economy even for the poor to purchase smaller quantities of an oleo-oil margarine if they cannot afford the luxury of real butter.'

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. In the case of 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.')

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

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

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 is stated in terms of alkali absorbed per mille. The number of grammes of the oil which would be saponified by 1 litre of normal solution of alkali is known as the 'saponification equivalent.'

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

Glyceride.	*Formula.*	*Molecular Weight.*	*Saponification Value.*	*Saponification Equivalent.*
Butyrin ..	$C_3H_5(O{\cdot}C_4H_7O)_3$	302	557	=100·67
Laurin ..	$C_3H_5(O{\cdot}C_{12}H_{23}O)_3$	638	264	=212·67
Palmitin ..	$C_3H_5(O{\cdot}C_{16}H_{31}O)_3$	806	209	=268·67
Stearin ..	$C_3H_5(O{\cdot}C_{18}H_{35}O)_3$	890	189	=296·67
Olein ..	$C_3H_5(O{\cdot}C_{18}H_{33}O)_3$	884	190	=294·67

The process is carried out as follows: About 2 grammes of the sample are accurately weighed out in a flask of about 200 c.c. capacity. This is then treated with 25 c.c. of alcoholic solution of caustic potash of approximately seminormal strength.* A like amount of the alkali is run into an empty flask for a blank experiment. It is not necessary that exactly 25 c.c. 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

* 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 treated with 1 per cent. caustic soda, either for two or three days in the cold, or for one or two hours under a reflux condenser, and then redistilled. When so treated the spirit darkens much less when boiled with potash.

of phenolphthalein are added to the flasks, the contents of which are titrated with exactly $\frac{N}{2}$ solution of hydrochloric acid. Each cubic centimetre of $\frac{N}{2}$ HCl used = 0·02805 of KHO; therefore the difference between the two titrations multiplied by this factor will give the amount of potash taken up by the oil.

The saponification value shows the number of milligrammes of potassium hydrate required for the saponification of 1 gramme of the oil. It is obtained by multiplying the percentage of KOH absorbed by 10. Thus, in the example given below the saponification value is 19·3 × 10 = 193.

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

Example—

Amount of oil taken	.. ..	2·001 grammes.
$\frac{N}{2}$ HCl for titrating back	..	12·2 c.c.
$\frac{N}{2}$ HCl required for 'blank'	..	26·0 c.c.
	Difference =	13·8 c.c.

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

$$= 290{\cdot}7 \text{ saponification equivalent.}$$

Free Fatty Acids.—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 are well shaken with about 100 c.c. of boiling neutral alcohol. A drop or two of phenolphthalein solution is added, and decinormal solution of NaHO run in with constant agitation, until a permanent pink colour is obtained. Each cubic centimetre of $\frac{N}{10}$ NaHO = 0·0282 oleic

acid. Oils intended for dietetic purposes should not contain much free acid. An acidity exceeding 3 per cent. (as oleic acid) renders an oil unfit for consumption. Cod-liver, olive, cotton-seed, and arachis oils can be procured commercially with less than 1 per cent.

The result is often stated as an 'acid value' which is 'the number of milligrammes of potassium hydroxide required to neutralise the free fatty acids in 1 gramme of the fat or oil.'

Determination of the Unsaponifiable Matter.—Five grammes of the sample are saponified with 50 c.c. of alcoholic potash of approximately seminormal strength by boiling under a reflux condenser for about thirty minutes, with frequent agitation. The solution is then evaporated down to dryness in a dish. The resulting soap is dissolved in about 200 c.c. 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 cubic centimetres 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. Especially when dealing with liver oils it is important to wash the ethereal solution very thoroughly, preferably first with sodium hydrate solution, and afterwards with water, to prevent a too high result being obtained owing to soap retained in solution. 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.

For solid waxes and lanolin, it is best to use Wilkie's method (*Analyst*, 1917, p. 200) where a mixture of 0·5 gramme of the wax and 4·5 grammes of castor oil is saponified and a correction applied for the unsaponifiable matter of the diluent oil.

Nature of the Unsaponifiable Matter.—This may consist of cholesterol, phytosterol, mineral oil, 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. Hydrocarbons, such as heavy mineral oil, may often be detected by the fluorescence which is imparted to the ethereal solution. Rosin oil may be detected by the bromide of tin test. (See under 'Colour Tests.') A hydrocarbon 'spinacene' has been found by A. C. Chapman in large proportions in some fish-liver oils.

Hübl's Iodine Absorption Equivalent.—All oils and fats are composed of glycerides 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. The amount of the halogen that can be combined would be dependent upon the amount of unsaturated acids in the oil.

The Hübl solution is made as follows: 25 grammes of iodine are dissolved in 500 c.c. 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 c.c. capacity. The oil is then dissolved in 10 c.c. of chloroform; when this has taken place, 25 c.c. of the Hübl reagent is added from a pipette. A blank experiment is also started, using the same quantities of chloroform and iodine solution. The bottles are then allowed to remain in the dark for not less than six hours if a solid fat or non-drying oil, for not less than eight hours if a semi-drying oil, or eighteen hours if a fish oil or drying oil. To the contents of the two bottles are added 20 c.c. of a 10 per cent. solution of potassium iodide and about 150 c.c. 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 cubic centimetres of thiosulphate used is deducted from the amount required for the blank experiment; the difference is multiplied by 0·0127 (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 c.c. $\frac{N}{10}$ $Na_2S_2O_3$
Sample required .. .. 18·0 c.c. ,,

Difference = 12·0 c.c. × 0·0127 =

$$\frac{0{\cdot}1524 \times 100}{0{\cdot}205} = 74{\cdot}34 \text{ per cent. } \textit{iodine absorbed.}$$

The thiosulphate solution must always be standardised before using against pure iodine to ascertain its exact strength. A substantial excess of Hübl (such as an amount of iodine equal to that absorbed) should be untouched at the end of the wait.

A modification of this process has been devised by Wijs. The iodine solution used is more stable, and a saving of time is effected: 8 grammes of iodine

trichloride and 8·8 grammes of iodine are dissolved separately in glacial acetic acid, and then poured into a litre flask and made up to a litre with glacial acetic acid. Other proportions of iodine trichloride and iodine have been recommended, but Dubovitz (*P.J.*, January 30, 1915) says they should be 7·8 grammes of iodine trichloride and 8·5 grammes of iodine per litre. In any case a slight excess of iodine, over that seen to be absorbed by the trichloride on mixing, is necessary. Bolton and Revis advise the heating of the solution in a water-bath for fifteen minutes to improve its keeping powers. The process is carried out in the same way as Hübl's method, but pure carbon tetrachloride is sometimes used instead of chloroform. With oils having an iodine value below 100 the reaction is complete in half an hour. Semi-drying oils should be given an hour. Wijs and Hübl values agree.

Yet another quick method is that of Hanus: An iodine monobromide reagent is prepared by dissolving 26 grammes of finely powdered iodine in 2 litres of glacial acetic acid and then adding 5 c.c. of bromine from a burette, so that, when potassium iodide is added, the final titre is double or slightly less than double the original titre. Glacial acetic acid is used as a solvent for resins and carbon tetrachloride for fats. When the value will be under 110, thirty minutes' contact suffices, but for higher values two hours should be allowed.

Maumené's Test.—This test depends on the rise of temperature which takes place on mixing oils with concentrated sulphuric acid (97 per cent.). The strength of the acid must be determined by titration. The specific gravity is useless in determining the strength of sulphuric acid; 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 test:

Fifty grammes of the sample are weighed out into a tall beaker of about 250 c.c. 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 c.c. of the 97 per cent. H_2SO_4 are 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 c.c. 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 that of the oil, but E. J. Bevan found that 5° difference do 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.

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.

Refractive Index.—Since the introduction of the Zeiss butyro-refractometer (see p. 75), the oleo-refractometer has been largely discarded, except for certain oils, such as rosin and tung oils, whose refractive indices are outside the butyro-refractometer scale. The correction of 0·55 scale division for each degree of temperature when testing butter by the butyro-refractometer is *not* applicable to other oils and fats. Generally for this instrument a standard temperature of 40° C. is used for fats solid at ordinary temperature. The readings of oils may be taken at 25° C., but when examining mixtures of fat and oil (*e.g.*, 'compound lard') their butyro-refractometer values at 40° C. are a convenience. The readings given on pp. 208 and 209 are the results of observations by W. Chattaway and ourselves.

Colour Tests.—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, and the following:

Hager's Test for Cholesterol.—A small fragment of cholesterol is dissolved in about 2 c.c. 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.

Olive Oil.

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

The free fatty acid varies very much in different samples. In 'salad' oil it should not much exceed 1 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 per cent. The Zeiss butyro-refractometer reading is remarkably constant.

The B.P. gives a limit of 6 for acid value and a test for arachis oil incapable of detecting less than 10 per cent. of the latter (Southall).

Adulterants would be detected as follows: Cotton-seed oil by the high figures obtained with the iodine absorption, butyro-refractometer, Maumené test, and specific gravity, also by the silver test and Halphen's 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,

Analytical Constants of Oils and Fats.

Oil or Fat.	*Specific Gravity at 15·5° C.*	*Saponification Value.*	*Iodine Absorption.*	*Valenta Test.*	*Butyro-refractometer at 25° C.*	*Maumené Test.*
VEGETABLE OILS.						
Non-drying oils :						
Olive	0·914 to 0·918	190 to 196	78 to 86	83° to 91°	61 to 63	40° to 45°
Almond ..	0·916 to 0·920	188 to 197	94 to 99	72° to 87°	64 to 65	51° to 54°
Peach-kernel	0·918 to 0·921	189 to 192	95 to 105	80° to 83°	—	40° to 46°
Arachis ..	0·917 to 0·921	190 to 196	83 to 102	72° to 74°	—	45° to 60°
Semi-drying oils :						
Cotton-seed ..	0·922 to 0·930	191 to 195	101 to 116	71° to 89°	68	74° to 80°
Sesame ..	0·921 to 0·924	188 to 193	106 to 110	90° to 97°	68 to 69	64° to 68°
Rape	0·914 to 0·917	175 to 178	99 to 105	77° to 83°	—	52° to 59°
Castor ..	0·960 to 0·966	178 to 186	83 to 86	Miscible	77 to 78	45° to 47°
Mustard ..	0·916 to 0·924	172 to 175	92 to 100	—	—	44° to 49°
Drying oils :						
Linseed ..	0·932 to 0·937	187 to 195	173 to 200	46° to 48°	79 to 81	104° to 120°
Hemp-seed ..	0·925 to 0·931	190 to 193	144 to 150	—	—	95° to 98°
Niger-seed ..	0·927 to 0·930	189 to 191	126 to 135	50° to 53°	—	81° to 83°
Sunflower ..	0·924 to 0·926	190 to 194	119 to 135	59° to 63°	—	67° to 75°

Analytical Constants of Oils and Fats—*Continued.*

Oil or Fat.	*Specific Gravity at 15·5° C.*	*Saponification Value.*	*Iodine Absorption.*	*Valenta Test.*	*Butyro-refractometer at 25° C.*	*Maumené Test.*
ANIMAL OILS.						
Neat's-foot ..	0·914 to 0·919	194 to 199	69 to 73	72° to 75°	—	47° to 49°
Lard oil ..	0·914 to 0·916	191 to 196	77 to 80	74° to 76°	—	65° to 67°
FISH OILS.						
Cod-liver ..	0·923 to 0·930	171 to 197	151 to 169	70° to 76°	77 to 80	113° to 116°
Whale	0·919 to 0·931	188 to 224	110 to 136	68° to 71°	—	86° to 90°
Seal	0·924 to 0·929	189 to 193	127 to 153	70° to 75°	—	90° to 95°
	Sp. Gr. $\frac{99° C.}{15·5}$				*Butyro-refractometer at 40° C.*	
VEGETABLE FATS.						
Palm Oil ..	0·858	196 to 202	52 to 57	—	—	—
Cotton stearin ..	0·864	195 to 196	89 to 92	—	—	—
Cacao butter ..	0·858	192 to 201	34 to 37	—	47	—
ANIMAL FATS.						
Butter-fat ..	0·865 to 0·867	221 to 232	23 to 38	29° to 39°	} See p. 77	—
Margarine ..	0·856 to 0·860	193 to 197	50 to 57	94° to 97°		—
Lard	0·860 to 0·862	195 to 197	50 to 65	97° to 99°		24 to 27·5°
Tallow	0·860	193 to 198	35 to 42	96° to 99°		—

and butyro-refractometer figures; rape oil by the butyro-refractometer, iodine absorption, Maumené and saponification tests.

A sample we examined consisted entirely of unsaponifiable oil (a mineral oil). It showed a slight green fluorescence, had a specific gravity of 0·8778, and gave Zeiss butyro-refractometer readings of 90° at 25° C., and 77° at 40° C.

A positive Baudouin test is unreliable. Sage (*P.J.*, 1915, p. 128) says Tunisian, Algerian, some Italian, and many Spanish oils give a very slight coloration with hydrochloric acid and sucrose; sufficient to suggest the presence of 5 per cent. of sesame oil in some cases.

Almond Oil.

Almond oil is expressed from the seed of the sweet and bitter almond-tree (*Prunus amygdalus dulcis* and *Prunus amygdalus amara*). Almond oil has a very pale yellow colour and bland taste. It is adulterated with peach-kernel, olive, sesame, cotton-seed, poppy, and arachis oils. Nearly the whole of the so-called 'foreign' almond oil consists of peach-kernel oil, the characters of which are so similar to those of almond oil that it is 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 are shaken with 1 part of the acid, when almond oil gives a light yellow colour, turning brown. Peach-kernel oil gives a bright red colour.

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 arachis oil, olein and palmitin are replaced by the glyceride

of arachidic acid. The isolation of this acid determines the presence of arachis oil when used as an adulterant of other oils.

Determination of Arachidic Acid.—The test of Bellier as modified by Mansfeld, Adler, Franz and Norman Evers (*Analyst*, 1912, p. 487) is used: Record must be kept of all amounts of 90 per cent. and 70 per cent. alcohol respectively used after the saponification. Five grammes of the oil are saponified for about five minutes under a reflux condenser with 25 c.c. alcoholic potash (80 grammes potash dissolved in 80 c.c. water and made to a litre with 90 per cent. alcohol). To the hot soap solution is added 7·5 c.c. of a mixture of one volume of glacial acetic acid and two volumes of water, and 100 c.c. of 70 per cent. alcohol containing 1 per cent. (by volume) of HCl, and the liquid is cooled to 12° to 14° C. for an hour. It is filtered and washed with 70 per cent. alcohol containing 1 per cent. HCl at 17° to 19° C. (the precipitate being broken up occasionally with a platinum loop) till the filtrate gives no turbidity with water. According to its bulk, the precipitate is dissolved in 25 to 70 c.c. hot 90 per cent. alcohol and cooled to 15° to 20° C. If crystals appear in any quantity, it is kept at this temperature for one to three hours, filtered, washed with 90 per cent. alcohol (about half the amount used for crystallisation), and finally with 50 c.c. of 70 per cent. alcohol. The crystals are washed into a weighed flask with warm ether, the ether is distilled off, and the residue dried at 100° C. and weighed. If the melting-point is lower than 71° C., it is recrystallised from 90 per cent. alcohol. Add to the weight thus obtained the quantity dissolved by the 90 per cent. alcohol used; 100 c.c. of which dissolve 0·022 gramme at 15·5° C., or 0·045 gramme at 20° C. Or, refer to Archbutt's table in 'Commercial Organic Analysis,' fourth ed., vol. ii., p. 94. Evers gives a table for the amount of arachidic acid dissolved in 70 per cent. alcohol used. The maximum correction is for a product melting at 71° C. and weighing over 0·1 gramme, when 0·013 gramme for every 100 c.c. of 70 per cent. alcohol used has also to be added to the quantity weighed.

According to whether the arachidic acid melts at 71° C., 72° C., or 73° C., the amount (corrected for solubilities in alcohol) is multiplied by 17, 20, or 22 respectively to give the corresponding amount of arachis oil.

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 c.c. of hydrochloric acid of specific gravity 1·2. To this is added 20 c.c. 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. Olive and cotton-seed oils bleached with 'lucidol' are said to react.

Tocher's Test.—One gramme of pyrogallol is dissolved in 15 c.c. of concentrated hydrochloric acid. This solution is well shaken in a separating funnel with 15 c.c. of the oil, and allowed to stand. After separation has taken place, the aqueous liquid is drawn off and boiled off 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 from the seeds of the *Brassica campestris*, and several allied plants. 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, cotton-seed, 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, but is insoluble in petroleum spirit. It is 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 from flax seeds (*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 oil 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 infrequently used as adulterants. As likely adulterants, Nash mentions: soja oil, sunflower oil, perilla oil, and wood oil.

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.

Cod-Liver Oil.

Particularly in seasons when cod are scarce, this oil is very liable to adulteration. The most prevalent form of adulteration is with the liver oils of other

fish, sometimes three or even more foreign liver oils being added. For this form of adulteration the 1898 B.P. colour test with sulphuric acid fails, as other liver oils give the violet colour. Moor pointed out that this test was not given from oil freshly extracted, as it apparently depends on products of decomposition. Most fish oils would not be detected by the specific gravity, but E. W. Mann approves a colour test, which, so far as is known, is only given by cod oil. It consists in adding 1 drop of a cooled mixture of 2 parts nitric and 1 part sulphuric acids to 15 drops of the oil. Before stirring, an orange-pink or brownish-pink colour is obtained, which, on stirring, changes to a vivid salmon-pink, not darkening to any considerable extent on standing. The Japanese cod oil gives a bright violet before stirring, and a greenish-brown after.

The percentage of free fatty acid should be low. A good class oil will not contain more than 0·5 per cent. (as oleic acid).

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. Wiley divides lards 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. The Chicago Board of Trade define choice lard as lard made from the 'leaf' and trimmings, rendered by steam heat.

Freshly rendered lard is quite free from free fatty acid. It possesses a pure white colour, a granular texture, and agreeable taste. Lard is extensively adulterated with cotton-seed oil, arachis oil, sesame oil, cotton-seed stearin, and beef stearin. We found

a sample to consist of coconut oil. Many of the so-called 'compound' lards do not contain any lard at all, being mixtures of cotton-seed oil and beef stearin.

The melting-point of lard ranges from 36° to 45° C. Other information will be found on p. 209. The iodine absorption and refractometer readings are most useful, but a normal iodine figure does not prove the sample to be genuine, as a judicious mixture of cotton-seed or arachis oil with cotton-seed or beef stearin would give normal figures.

The Silver Test for Cotton-seed Oil.—The Becchi test detects as little as 1 per cent. of cotton-seed oil. The reagent is made as follows: 1 gramme of finely-powdered nitrate of silver is dissolved in 100 c.c. of 95 per cent. alcohol; when dissolved, 20 c.c. of ether and 1 drop of nitric acid are added; 2 c.c. of this reagent are well shaken with 10 c.c. of the oil to be examined, and placed in boiling water for ten minutes. Any blackening due to reduced silver proves the presence of cotton-seed oil. Lard usually gives a very pale brown tint.

When this test is applied to olive oil, a brown coloration is sometimes obtained in the absence of cotton-seed oil. Tolman (*Analyst*, 1902, p. 198) gives a preliminary treatment, which we have found satisfactory in removing this uncertainty. To 25 c.c. of the oil, 25 c.c. of 95 per cent. alcohol are added, and the whole is then gently heated and vigorously shaken; after allowing the liquids to separate, the alcoholic solution is decanted off, and the residue washed, first with 2 per cent. nitric acid, and finally with water. This preliminary treatment can also be applied to lard and other fats.

Halphen's Test.—Equal volumes (5 c.c.) of the oil under examination, amyl alcohol, and carbon disulphide containing 1 per cent. of dissolved sulphur, are heated in a stoppered bottle in a water-bath for an hour. The stopper is tied in with string, and the bottle may be suspended in the boiling water or brine by means of a piece of string tied round the neck. It is seldom that the bottles break. A pink colour shows the presence of cotton-seed oil. As little as 1 per cent. of cotton-seed oil can be detected.

Halphen's test fails if the amyl alcohol be carefully purified. Gastaldi substitutes pyridine and makes the test more sensitive as follows: 5 c.c. of oil are treated with 1 drop of pyridine and about 4 c.c. of carbon disulphide containing 1 per cent. of sulphur, and the mixture is heated on the water-bath.

If the cotton-seed oil has been previously heated, no coloration will be obtained with Halphen's reagent. If hydrogenised, it gives a less pronounced colour. Southall Bros. and Barclay found the silver test less disturbed by heat, while Bird and Lucas's test (the brown coloration produced by shaking with an equal volume of nitric acid, specific gravity 1·375) was also given by heated cotton-seed oil. The lard from hogs fed on cotton-cake will give Halphen's reaction.

Water.—Lard should 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.

Chlorides.—Pure lard contains only traces of chlorides. In seventeen samples we analysed the chlorine figure ranged from 0·001 to 0·014 per cent. It is estimated by melting together 50 grammes lard and 50 c.c. distilled water in the water-oven, thoroughly stirring, and titrating an aliquot part of the aqueous extract with standard silver nitrate solution (4·79 grammes per litre; 1 c.c. = 1 milligramme chlorine).

'Compound' lards sometimes contain excessive amounts.

Paraffin Wax to the extent of 2 or 3 per cent. is sometimes added. It will be found in the 'unsaponifiable matter.' It may be detected by Holde's test: 10 drops of the melted fat are saponified in a test-tube with 5 c.c. of approximately semi-normal alcoholic potash, and to the clear hot soap solution water is added in successive quantities of about 1 c.c., the solution being carefully observed after each addition of water. While pure lard gives a clear solution of soap after dilution with 5 c.c. of water, the presence of 0·5 per cent. of paraffin wax is indicated by the formation of a turbidity, the 'silky' appearance

of which is characteristic of paraffin wax (Dunlop, *Analyst*, December, 1909).

Beef Stearin.—W. F. K. Stock 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° C., 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° C., 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 c.c. of the melted fat are run into a graduated cylinder of about 25 c.c. capacity; 21 c.c. of ether are added, and the fat dissolved at 20° to 25° C.; 3 c.c. 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 c.c. of fresh ether at 13° C. are 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 40° 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 at 45·8° C. gave, however, 0·146 gramme of crystals.

NOTES ON THE BRITISH PHARMACOPŒIA

The British Pharmacopœia is prepared by the General Medical Council under the authority of the Medical Act of 1858, section 54.

Section 15 of the Pharmacy Act, 1858, enacted that: 'Any person who shall . . . compound any medicine of the British Pharmacopœia except according to the formularies of the said Pharmacopœia, shall for every such offence be liable to pay a penalty or sum of Five Pounds.' It is, however, in connection with the Sale of Food and Drugs Acts that the Pharmacopœia is chiefly invoked as establishing the composition of any article included therein. Except where it is obviously at fault, its requirements are consistently upheld by the courts of law. Reference should therefore always be made to the Pharmacopœia in the analysis of any drug named therein.

Many articles whose names figure in the Pharmacopœia are also sold, often in a less pure condition, for purposes other than that of internal administration. Where confusion is possible, it is the duty of the analyst to afford protection to the public, and to avoid injustice to the vendor by a careful and unbiassed portrayal of the issues involved, so that they are plain to the authority administering the Acts, and to the Justices in the event of action ensuing.

The characters of many Pharmacopœial articles having already been given, reference should be made to the index before concluding that they are not dealt with.

The edition of the British Pharmacopœia at present in use is that of 1914.

The Tinctures of the British Pharmacopœia.

Specific Gravity.—This is obtained by use of bottle or Westphal balance, the temperature of the samples being brought to 15·5° C.

Total Solids.—On account of the natural variation of drugs, the total solids obtained by evaporating

the official tinctures to constant weight do not absolutely accord, but it is possible to lay down limits within which all genuine samples should fall.

In the case of a good many B.P. liquid preparations, concentrated articles to be diluted with the requisite strength of alcohol in order to produce the Pharmacopœial article are sold, particularly in the case of infusions, in which the concentration is as much as seven times. Many of these tinctures, etc., when made up, do not contain the same amount of solids as a tincture which has not been concentrated, and their use is, for this reason, to be deprecated.

Estimation of Alcohol in Tinctures, Liniments, etc.—Owing to the viscosity of most tinctures, it is impossible to obtain a correct figure for the alcohol by merely pipetting out 25 c.c., making up to 125 c.c., and distilling over 100 c.c. To overcome this difficulty, the following procedure is resorted to: A 100 c.c. flask is taken, and a 25 c.c. pipette, preferably with the bulb at the lower end, to offer less surface for the tincture to cling to, is used. Into the 100 c.c. flask four lots of approximately 25 c.c. are pipetted in the following way: The liquid is drawn up to the usual mark, and then allowed to run into the 100 c.c. flask while the liquid runs in an uninterrupted stream, and the pipette quickly removed before the first separate drop falls. When the flask has been more or less filled to the mark by repeating this treatment four times, the pipette is again filled with the tincture, and this is allowed to go into the flask drop by drop, the drops being counted, until the mark is reached. A quantity of 25 c.c. is now allowed to run into the distillation-flask in the manner used before without allowing the introduction of a separate drop, and then a quarter the number of drops needed to bring the liquid up to the mark in the 100 c.c. flask is added. By this means we ensure getting in the distillation-flask exactly one-quarter the volume of the 100 c.c. One hundred c.c. of water are added and a few pieces of pumice, and the liquid is distilled till 100 c.c. of distillate are collected. The distillate flask is then corked and put in a bath at 15·5° C., and allowed to cool to this temperature. Distilled water is added

to bring the liquid to the 100 c.c. mark, the gravity is taken by means of a bottle, and the percentage of alcohol corresponding to this gravity looked up in the tables. The percentage of alcohol found is then multiplied by 4, in order to get the percentage in the tincture. This process will apply to all the tinctures, liniments, liquid extracts, infusions, and succi of the Pharmacopœia, but certain of them contain constituents calling for special treatment, which are given below.

Preparations of digitalis, squills, quillaia, euonymus, belladonna, eucalyptus, aloes, ergot, and senega, froth to a greater or less degree, which can be to a great extent counteracted by the addition of a little tannin to the distillation-flask. In the cases of sarsaparilla and strophanthus preparations tannin has but little effect, and using a small flame is the only way to prevent the froth getting in the condenser, or a test-tube brush may be suspended in the neck of the flask to break up the froth.

Aconite, belladonna, ammoniated camphor, opium and soap liniments, and tinct. camph. co. contain camphor, which distils over and is removed by passing the distillate through a dry filter-paper after making up to 100 c.c. and mixing. Thorpe's petroleum ether method can also be employed.

The ammoniacal tinctures of valerian, ergot, guaiacum, opium, and quinine should first be neutralised with dilute sulphuric acid or tartaric acid, and the same step must be taken when dealing with sal volatile and ammoniated liniment of camphor.

To tinct. iodi fort. and to tinct. iodi mitis sufficient sodium thiosulphate must be added to decolourise the liquid, which is then neutralised with NaOH.

To tinct. ferri perchlor. sodium carbonate must be added to prevent any hydrochloric acid distilling over. To tinct. benzoin. co. caustic soda should be added to prevent any benzoic acid coming over.

The liniments which contain soap should be treated with tartaric acid till a white precipitate is produced.

The compound tincture of camphor has to be specially treated, as detailed below, owing to the

presence of camphor and the large quantity of essential oil.

Fifty c.c. of the sample are taken, and made up to 350 c.c. 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 c.c. with water, filtered through a dry filter, and 250 c.c. of the filtrate distilled until about 200 c.c. have passed over. The distillate is then made up to 250 c.c. and the specific gravity taken at 15·5° C. If the foregoing instructions be adhered to, the percentage of alcohol corresponding to the specific gravity of the distillate, multiplied by 8, will be the percentage by volume contained in the tincture.

A loss of spirit is unavoidable in the manufacture of tinctures, and the moisture natural to drugs may in some tinctures also tend to lower the percentage of alcohol in the finished product. It is therefore not possible to lay down a hard-and-fast rule as to the deficiency of alcohol that may reasonably be passed, but we think that in no tincture ought this loss to exceed 3 per cent. of absolute alcohol by weight.

Methylic Alcohol.—Methylated spirit is sometimes used partly or wholly in the preparation of tinctures, etc. This can be tested for by the Riche and Bardy test as given under 'Spirits.'

T. Aconiti.—The total solids are about 2 grammes per 100 c.c. The root of the *Aconitum napellus* is directed to be used. There is no chemical means of ascertaining whether the true root has been used in making galenical preparations. An official process is provided for the estimation of the ether-soluble alkaloids, which must amount to 0·04 gramme per 100 c.c.

T. Alstoniæ.—Data not yet available.

T. Arnicæ Florum.—The specific gravity is about 0·950, the total solids about 2·3 per cent. w/v, and the alcohol about 45 per cent. by volume (Squire).

T. Asafetidæ.—The solids should be about 10 per cent., and the alcohol about 66 per cent. The specific gravity is about 0·913.

Samples have been found very low in solids, owing to the use of gum containing high quantities of mineral matter.

T. Aurantii.—The solids should be not less than 1·8 per cent., the specific gravity about 0·880, and the alcohol about 74 per cent.

T. Belladonnæ.—The solids are of small consequence in this tincture, as it is standardised officially, and must contain 0·035 gramme of alkaloids calculated as atropine, in 100 c.c.

T. Benzoini Co.—The solids should be about 18 grammes per 100 c.c., and the alcohol about 68 per cent. If the solids are low, it is probably due to the use of a benzoin containing much insoluble matter.

Barclay and Mann (*Chemist and Druggist*, March 15, 1902) give a process for standardisation, and suggest that the tincture, when assayed by that process, should yield 'not less than about 5 per cent. of balsamic acids calculated as benzoic, out of which neither more or less than about two-fifths should be present in an uncombined condition.'

T. Berberidis.—Data not yet available.

T. Buchu.—The solids should be about 3·8 grammes per 100 c.c., and the alcohol about 56 per cent.

T. Calumbæ.—The solids should be about 1 gramme per 100 c.c., and the alcohol about 56 per cent.

T. Camph. Co.—This tincture ought to contain 0·05 gramme of anhydrous morphine in 100 c.c. The total solids vary curiously in commercial samples. The alcohol should be about 58 per cent. The British Pharmacopœia does not prescribe any method of assay, but directs that it shall be made with the officially standardised tincture. To attempt the assay on much less than 200 c.c. is very likely to produce misleading results.

The proportion of opium 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.

The tint obtained is compared with that given by a sample of known quality.

The benzoic acid can be estimated as follows: 25 c.c. of the tincture are rendered alkaline with sodium hydrate, and evaporated to 10 c.c.; a portion of the camphor and oil of anise will be volatilised. 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 $\frac{N}{10}$ NaHO, using phenolphthalein as indicator. Ten c.c. of the tincture is a convenient quantity to titrate. Each cubic centimetre of the soda required = 0·0061 benzoic acid.

T. Cannabis Indicæ.—The solids should be about 4 grammes per 100 c.c., and the alcohol about 86 per cent.

T. Cantharidini.—This is prepared by dissolving 0·1 part of cantharidin in 10 parts of chloroform and sufficient 90 per cent. alcohol to make 1,000. It therefore should contain 0·01 gramme of total solids per 100 c.c.

The beetles contain amounts of cantharidin varying from 0·5 to 1 per cent., with an average possibly of about 0·8 per cent.

T. Capsici.—The solids vary from about 0·7 to 1·5 gramme per 100 c.c. The alcohol is about 58 per cent. by volume.

T. Cardam. Co.—The present tincture contains about 13 grammes of total solids in 100 c.c., or twice those of the 1898 tincture. This is due to the substitution of glycerin for raisins. The alcohol content has dropped.

T. Cascarillæ.—The tincture should contain not less than 1·6 grammes of resin per 100 c.c. (Barclay). The alcohol is about 66 per cent.

T. Catechu.—The solids should not be less than 14 grammes per 100 c.c.

T. Chiratæ.—The solids should be about 1 gramme per 100 c.c., and the alcohol about 57 per cent.

T. Chlorof. et Morph. Co.—Except for the presence of an extra minim of oil of peppermint per 4 ounces, this is identical with the 1898 article.

T. Cinchonæ.—Officially standardised, to contain 1 gramme of alkaloids per 100 c.c. The alcohol is about 64 per cent.

T. Cinchonæ Co.—Officially standardised, to contain half the alkaloids of the simple tincture. The cochineal has been slightly reduced and saffron is omitted.

T. Cinnamomi.—The solids should not be less than 2·2 grammes per 100 c.c. The alcohol is about 68 per cent.

T. Cocci.—The solids should not be less than 2·5 grammes per 100 c.c. The alcohol is about 44 per cent. Some samples of cochineal are weighted with French chalk, oxide of iron, etc.

T. Colchici.—The solids vary considerably. Though not officially standardised, the tincture should contain not less than 0·05 gramme of colchicine per 100 c.c.

T. Cubebæ.—Barclay suggests 2 grammes per 100 c.c. of oleo-resin as a standard. Commercial samples do not always come up to this.

T. Daturæ Sem.—Data not yet available.

T. Digitalis.—The solids are about 2·5 grammes per 100 c.c.

T. Ergotæ Ammon.—The specific gravity ranges from 0·931 to 0·938; the total solids should be 4 grammes per 100 c.c., and the alcohol by volume about 50 per cent.

T. Ferri Perchlor.—'Tincture of iron' under this name does not occur in the B.P., and therefore, as a technical point, there may be thought to be no definite composition required. In practice, however, tincture of ferric chloride, which is a Pharmacopœial preparation, is always supplied when tincture of iron is asked for. Tincture of ferric chloride is a mixture of 1 volume of strong solution of ferric chloride with 1 volume of 90 per cent. alcohol, and

sufficient distilled water to make 4 volumes of tincture. Strong solution of ferric chloride (1914) containing 20 per cent. w/v of iron, tincture of ferric chloride should contain 5 grammes per 100 c.c. The determination is made in the usual gravimetric manner by precipitation with ammonia. The precipitate being bulky, 5 c.c. of the tincture diluted to, say, 50 c.c. with water is quite a suitable quantity on which to work. This quantity should yield 0·355 gramme of iron oxide.

T Gelsemii.—Barclay suggests 0·025 gramme per 100 c.c. of total alkaloid. The alcohol is about 58 per cent.

T. Gentianæ Co.—The solids are about 5 grammes per 100 c.c., and the alcohol about 43 per cent.

T. Guaiaci Ammon.—The solids should be not less than 15 grammes per 100 c.c., and the alcohol about 72 per cent.

T. Hamamelidis.—The solids are about 2 grammes per 100 c.c., and the alcohol about 44 per cent.

T. Hydrastis.—Though not itself standardised, this is prepared from the standardised liquid extract, and may be presumed to contain about 0·2 gramme of hydrastine per 100 c.c.

T. Hyoscyami.—Squire says the specific gravity is about 0·899, the total solids 3 per cent. w/v, and the alcohol 70 per cent. by volume.

T. Iodi Fortis.—This is weaker than the 1898 B.P. liq. iodi fortis, which it replaces. It is required to contain not less than 9·75 nor more than 10 per cent. of iodine as determined by titration with thiosulphate.

T. Iodi Mitis.—The specific gravity varies from 0·878 to 0·882, and the alcohol from 85 to 88 per cent. by volume (see p. 220). The B.P. requires from 2·44 to 2·51 per cent. of iodine, which, being determined by titration with thiosulphate, will not include any hydriodic acid present. Lormand (abst. *Journ. Chem. Soc.*, 1915, ii., 103) says hydriodic acid is always present.

T. Jalapæ.—Officially standardised (1·5 grammes resin per 100 c.c.). The alcohol is about 68 per cent.

T. Jalapæ Co.—Squire gives the specific gravity as about 0·924 and the total solids as about 4 per cent. w/v.

T. Kaladanæ.—No data yet available.

T. Kino.—The specific gravity ranges from 0·994 to 0·998, the total solids from 23 to 27 grammes per 100 c.c., and the alcohol by volume is about 50 per cent.

T. Krameriæ.—The solids should be about 5 grammes per 100 c.c. The alcohol is about 56 per cent.

T. Lavandulæ Co.—No data yet available.

T. Limonis.—The solids should be not less than 1·5 grammes per 100 c.c. The alcohol is about 75 per cent.

T. Lobeliæ Ætherea.—No data on new tincture are yet available. The ether used in spirit of ether is now 0·720, in the 1898 B.P. it was 0·735.

T. Myrrhæ.—The solids should not be less than 5·5 grammes per 100 c.c. The alcohol is about 84 per cent.

Large variations in the solids have been observed in commercial tinctures, probably due to the use of myrrh containing much matter insoluble in alcohol. The alcohol is about 85 per cent.

T. Nucis Vomicæ.—A content of 0·125 gramme of strychnine per 100 c.c. is officially required. H. R. Jensen (*P.J.*, 1916, 458) criticises the hot nitration method of the B.P., and recommends a temperature of 20° C. provided the nitric acid is 'active.'

T. Oliveri Corticis.—No data yet available.

T. Opii (*Laudanum*).—The solids vary a good deal naturally. It is required to yield 1 gramme of morphine calculated as anhydrous per 100 c.c. The official method of assay works well if the quantities are adhered to, but serious errors arise if smaller quantities are employed.

T. Opii Ammon.—This contains 10 per cent. of t. opii and 20 per cent. of solution of ammonia by volume.

T. Picrorhizæ.—No data yet available.

T. Podophylli.—The solids should be not less than 3·6 grammes per 100 c.c. The alcohol is about 86 per cent.

T. Podophylli Indici.—No data yet available.

T. Pruni Virg.—Glycerin now enters into the composition.

T. Pyrethri.—The alcohol is about 68 per cent. The specific gravity is about 0·900 and the solids usually about 2 per cent. w/v, though sometimes they are very much lower.

T. Quassiæ.—The solids vary a great deal. The alcohol is about 44 per cent. Barclay proposed 0·05 gramme of quassin per 100 c.c. as a standard.

T. Quillaiæ.—The specific gravity varies from 0·918 to 0·924, the total solids are about 1·2 grammes per 100 c.c., and the alcohol about 58 per cent. by volume.

T. Quininæ.—The specific gravity is about 0·890, and the total solids about 3·6 grammes per 100 c.c.

T. Quininæ Ammon.—The total solids are about 1·8 grammes per 100 c.c. and the alcohol about 53 per cent.

T. Rhei Co.—Squire gives the solids as about 17·5 per cent. w/v, which is appreciably higher than we ever found on the old tincture, so presumably the 45 per cent. alcohol now used extracts more than the 60 per cent. of the 1898 B.P.

T. Scillæ.—The solids should be not less than 10 grammes per 100 c.c. The alcohol is about 54 per cent.

T. Senegæ.—The solids vary from 4·7 to 6·5 grammes per 100 c.c., and the alcohol is about 56 per cent. by volume.

T. Sennæ Co.—Glycerin is now used in place of raisins. The alcohol is about 36 per cent.

T. Serpentariæ.—The solids should not be less than 2 grammes per 100 c.c. The alcohol is about 57 per cent.

If the solids are lower than 2, it is probably due to the use of a drug containing much earthy matter. The ash of the drug ought not to be more than 10 per cent., but some samples have been found to carry sand and earth up to double this figure.

T. Stramonii.—Barclay suggests 0·04 gramme per 100 c.c. of total alkaloid as a standard. The alcohol is about 42 per cent.

T. Strophanthi.—There is frequent admixture of non-official strophanthus seeds with the official variety. See Moor and Priest (*Analyst*, xxvi., p. 33);

also E. M. Holmes (*Pharm. Journ.*, iv., xiv., 254). The genuine tincture should yield distinct streaks of a greenish colour if 2 c.c. are evaporated to dryness in a white dish and the residue spotted with 80 per cent. sulphuric acid. The alcohol should be about 67 per cent.

T. Tolutana.—The solids should be not less than 8·5 grammes per 100 c.c. Barclay suggests as a standard 3 grammes per 100 c.c. of balsamic acid, one third of which are free. The alcohol is about 81 per cent.

T. Urgineæ.—No data yet available.

T. Valerianæ Ammon.—The solids should be not less than 3 grammes per 100 c.c. The alcohol is about 53 per cent.

T. Valerianæ Indicæ Ammon.—No data yet available.

T. Zingiberis.—The solids should be not less than 0·4 gramme per 100 c.c. The alcohol is about 87 per cent.

MISCELLANEOUS PHARMACOPŒIAL ARTICLES

Camphorated Oil (*Linimentum Camphoræ*).—This is prepared by dissolving 1 part by weight of camphor in 4 parts by weight of olive oil. The camphor may be approximately determined by taking the specific gravity, which should fall between 0·924 and 0·927. Leonard and Smith (*Analyst*, 1898, p. 281) have calculated that each per cent. of camphor raises the gravity by about 0·00045. The camphor may be accurately estimated by heating 5 grammes of the oil in a flat-bottomed dish for two hours at 120° C. Leonard and Smith have shown that olive oil treated in the same way *gains* 0·15 per cent. in weight. This figure added to the loss in weight shows the true amount of camphor.

The camphor can also be estimated by determining the rotation of the sample in a polarimeter. The angular rotation per 100 millimetres multiplied by the factor 1·962 gives the percentage of camphor in the sample (Dowzard). The camphor only slightly

interferes with the refractive index of the olive oil, our own experience being that the original sample will read about one degree lower on the Zeiss butyro-refractometer scale than the camphor-free oil will.

The olive oil is sometimes wholly or partly replaced by mineral or cotton-seed oils. Partial substitution of the camphor by mineral oil volatile at 120° C. has been reported.

Little loss of camphor takes place on keeping.

Sandal-Wood Oil.—The B.P. requires a specific gravity of 0·973 to 0·985; an optical rotation of −13° to −21°; a refractive index (25° C.) of 1·498 to 1·508 (*i.e.*, on the Zeiss butyro-refractometer the whole field is bright); solubility of 1 volume in 6 volumes of 70 per cent. alcohol at 20° C. (which excludes very old oils and, according to Evans, 1912, some freshly distilled oils), and 90 per cent. of total alcohols calculated as santalol.

Eucalyptus Oil.—The B.P. requires a specific gravity of 0·910 to 0·930 (occasionally genuine oils fall below 0·910); an optical rotation of −10° to +10°; and 55 per cent. of cineol (eucalyptol). No figure for refractive index is given, but we find that Zeiss butyro-refractometer readings at 25° C. run from 49° to 54°.

Sweet Spirits of Nitre (*Spiritus Ætheris Nitrosi*).—Five c.c. of the sample are run into a brine-charged nitrometer, followed by 5 c.c. potassium iodide solution, followed by 5 c.c. dilute sulphuric acid (10 per cent.) added in portions. When cool and the levels balanced, the volume of nitric oxide should not be more than 35 nor less than 20 c.c. This corresponds to a range of 1·52 to 2·66 per cent. by weight of ethyl nitrite.

The specific gravity should be between 0·838 and 0·842.

In summer the sale of sweet spirits of nitre is slower than in winter, and the tendency to decomposition (due to warmth and light) is greater. It should be dispensed from small bottles—say, 4-ounce bottles—closely stoppered, which should be kept in a cool and dark place.

Glycerin.—Water is readily absorbed from the air and is a likely adulterant. Though usually revealed by the specific gravity falling below 1·260, W. H. Roberts reported a sample where 11 per cent. of water and 14 per cent. of cane-sugar were present. In these proportions the mixed adulterants have a specific gravity of 1·260.

Liquid Paraffin.—The B.P. range of specific gravity is 0·860 to 0·890, Squire giving 0·865 to 0·890. The refractive index at 15° C. varies from 1·4706 to 1·4849 (Evans).

The *Lancet* (1915, October 2 and 16; 1916, August 12) urges the adoption for medicinal purposes of a minimum viscocity of 105 seconds at 100° F. (measured in Redwood's standard viscometer), because too thin an oil is neither a suitable nor safe lubricant for the digestive tract.

Syrup of Squill.—Total solids will be about 68 grammes per 100 grammes, and acetic acid about 1·1 grammes per 100 c.c. Squire gives the specific gravity as about 1·344.

Spirit of Sal Volatile.—The specific gravity should be between 0·888 and 0·893. Titration with normal sulphuric acid must show the equivalent of 2·16 grammes NH_3 per 100 c.c. A new B.P. test is required to show between 2·35 and 2·51 per cent. w/v of acid ammonium carbonate and ammonium carbamate.

Quinine Wine.—This contains 1 grain of quinine hydrochloride in 1 fluid ounce of orange wine. Its alcohol content is practically that of the orange wine, 12 to 14 per cent. by volume. The specific gravity is 1·044 to 1·095 (Squire). Salicylates and sulphites should be looked for.

Chamomile Flowers.—The dried, expanded flower-heads of *Anthemis nobilis*. The colour should be nearly white or only faintly buff, to exclude stale, badly dried, or damaged flowers. The ash should not exceed 5 per cent.

Powdered Rhubarb.—The ash of rhubarb root is usually from 7 to 12 per cent., though some samples may yield nearly 30 per cent. (Chattaway and Moor, *Analyst*, 1903, p. 207). The B.P. limit for ash is

15 per cent. Foreign starch should be looked for, but a starch natural to rhubarb root should not be forgotten.

Ipecacuanha Root.—The Rio root is alone official, and may be distinguished from the Carthagena by the official description given in the B.P.

The ash of the root is about 3 per cent., the B.P. specifying 5 per cent. as a maximum.

An official process for assay requires the presence of 2 per cent. of total alkaloids, a requirement that not 50 per cent. of consignments fulfil. The root must first be ground, and properly proportionate quantities of both must be employed, so as not to allow a separation of the woody fibre from the powder of the bark, the latter being richer in alkaloids. Gadd (*Analyst*, 1915, p. 304) discovered a mistake in the B.P. directions, insufficient acid to neutralise the ammonia being added.

Ipecacuanha Wine is prepared by adding 1 part of the official liquid extract to 19 parts of sherry, and, after being set aside for forty-eight hours, is filtered.

Different samples produce varying amounts of precipitate, and it is advisable that a detannated sherry should be employed. It also appears that some samples diminish in alkaloidal strength on keeping.

There is no official process for the assay of the wine, but it may be assayed by taking not less than 100 c.c., evaporating off most of the alcohol, and using the official process for the liquid extract. If the alkaloids are found to be less than 0·1 gramme per 100 c.c., the assay should be repeated, using the method published by Bird (*Pharm. Journ.*, 1900, 414).

Lime-Water.—It is specified that 24 c.c. shall require 10 c.c. of decinormal sulphuric acid for neutralisation (phenolphthalein is a suitable indicator), and that the sample shall yield no characteristic reaction for lead or for chlorides. The Pharmacopœial directions do not allow sufficient time for the attainment of a saturated solution (Kemsey-Bourne, *P.J.*, 1915, p. 522).

Crushed Linseed is linseed recently reduced to a coarse powder. It should yield not less than 30 per

cent. of oil when exhausted by carbon bisulphide, and the residual powder should show no starch when examined microscopically. It should not yield more than 5 per cent. of ash.

Exhausted or partially exhausted linseed is sold. Cruciferous seeds would be detected microscopically and by their odour on mixing with warm water. Linseed always contains a few foreign seeds from the harvesting.

Compressed Drugs.—A. E. Parkes found large amounts of talc in various tablets (indigestion tablets, aspirin, bismuthated magnesia, soda-mint), and regards 1 or 2 per cent. as the allowable maximum (*L.*, 1917, i., 809).

Santonin Lozenge.—Each lozenge contains 0·06 gramme of santonin. Old lozenges appear to have little vermicidal action and McWalter (*B.* and *C.D.*, 1907, December 13) says they yield but little trace of santonin when treated with alcohol. He finds chloroform ineffective for the extraction of santonin, and estimates it by treating a powdered lozenge with alcohol, striking a pink colour with ethyl nitrite and potassium hydroxide and comparing with the colour produced by pure santonin similarly treated. The pink colour quickly changes to a canary-yellow tint, but the intensity of either shade appears to depend on the quantity of santonin present.

Caffeine Citrate.—The B.P. gives a process for the estimation of the caffeine: 1 gramme is shaken with hot distilled water containing sufficient NaOH to give a distinctly alkaline reaction. Self (*P.J.*, 1915, p. 384) proposes a definite volume of say, 20 c.c., for fear caffeine would not all be extracted were a larger volume used. After cooling, three successive quantities of 10 c.c. each of chloroform are used for extraction, and when evaporated should yield 0·45 gramme of caffeine.

Quinine.—When this is asked for, quinine sulphate is usually supplied. Among B.P. tests is one requiring 1 gramme to dissolve in 7 c.c. of a mixture of 2 volumes chloroform and 1 volume absolute alcohol. We have never found solution to result in the cold, but it readily occurs on warming to 45° C.

Glauber's Salt.—The B.P. requires this to contain about 99·9 per cent. of $Na_2SO_4.10H_2O$, as determined from an SO_4 estimation. As the article readily effloresces in air a sample may satisfy the test and still contain appreciable impurities. Sodium chloride is the commonest impurity.

Epsom Salts. — $MgSO_4.7H_2O$, as calculated from an estimation of magnesium, is required to amount to from 97·4 to 100·0 per cent. Magnesium chloride is the commonest impurity.

Flowers of Sulphur.—An aqueous extract from 10 grammes of the sample must not require more than 5 c.c. decinormal NaOH. This permits an acidity as H_2SO_4 of 0·25 per cent., a figure that Evans (1909) found to range from 0·01 to 0·12 per cent. Their figures for ash ranged from 0·08 to 0·1 per cent., showing the B.P. limit of 0·25 to be generous. The arsenic estimation for which a special test is given is important, as large quantities are sometimes taken by persons and animals. Southall's (1912) find sublimed and roll sulphur to contain as a rule much less arsenic than precipitated sulphur.

Diatomaceous earth to be used in the proportion of 10 or 15 per cent. has been offered as an adulterant (*Y.B.P.*, 1912, p. 161).

Ammonium Carbonate.—It is said that even the freshly powdered article will never satisfy the official requirements (Southall).

Gregory's Powder is prepared by mixing—powdered rhubarb root, 2 parts; magnesia (light), 6 parts; powdered ginger, 1·1 parts.

The powder is liable to absorb carbon dioxide from the air, but even if kept for a considerable time it should not contain more than 5 per cent. of carbonate. Carbonate of magnesia has been employed instead of the oxide. The ash of a properly prepared powder is *about* 64 per cent., whereas a powder made with the carbonate yields an ash of *about* 27 per cent.

A microscopical examination should be made. The sample under examination and one prepared from known materials should be exhausted with 60 per cent. alcohol, and the extracts evaporated and weighed. This will show if exhausted rhubarb has been used.

Saffron.—Though not included in the 1914 edition, saffron was official in the 1898 B.P., where it was described as 'the dried stigmas and tops of the styles of *Crocus sativus*.' Rubbed on the wet finger, it was required to impart an intense orange-yellow tint, not to deflagrate when incinerated (absence of nitrates), not to deposit any powder when placed in water, not to leave more than 7 per cent. of ash, and not to contain more than 12·5 per cent. of moisture. When pressed between folds of white filter-paper, it was required to leave no oily stain.

Saffron dries rapidly, and the estimation of moisture requires to be started as soon as received.

The following have been used as adulterants: Safflower, crocus stamens, dyed marigold leaves, rootlets of carex, exhausted saffron, glycerol *cum* formaldehyde, invert sugar, sucrose, and mineral weighting substances, often caused to adhere by the addition of gum; barium sulphate, borax, potassium nitrate, sodium sulphate, magnesium sulphate, or alum.

A sample of 'Alicante' saffron examined by us was found to contain 25 per cent. of ash. Over two-thirds of this was added mineral matter, and, in addition, the sample contained dyed vegetable fibres.

Every fragment of genuine saffron, on being touched with strong sulphuric acid in a white dish, will afford a deep transient blue colour. Pierlot says that when a nitrate is present, a peach coloration, changing to light rose, is obtained.

Genuine saffron should afford but little colour to ether or petroleum spirit.

Saffron, when treated in the cold with 60 per cent. alcohol, should yield over half its weight of extractive matter.

One part of saffron agitated with 100,000 parts of water should cause the liquid to acquire a distinct yellow colour.

Compound Liquorice Powder (*Pulvis Glycyrrhizæ compositus*, B.P.) is a mixture of senna, 4; liquorice root, 4; fennel fruit, 2; sublimed sulphur, 2; refined sugar, 13. The 1898 B.P. formula differed in the proportion of sugar, which would have been 12 parts

(*i.e.*, 4 per cent. difference). The effects on analytical data are to raise the proportions of sugar and extractive yielded to 70 per cent. alcohol; other determinations are not appreciably affected.

The moisture should not exceed 6 per cent. The total ash should be between 4·0 and 5·5 per cent. Though the soluble ash is fairly constant (2·3 to 2·9 per cent.), J. Evans (*Pharm. Journ.*, 1905, 363) has shown it not to be a scientific criterion, as the sulphur converts some of the insoluble into soluble ash.

Extractives determined by macerating 5 grammes in 20 c.c. of 70 per cent. alcohol for forty-eight hours and percolating to yield about 60 c.c. (C. G. Moor and J. E. Kirkpatrick, 'Suggested Standards') amount to about 63 per cent.

Sublimed sulphur is often only partially soluble in carbon disulphide, and extraction with the latter is not advised. Sulphur can be estimated by Alcock's method: 1 gramme of the powder is treated with fuming nitric acid and a little potassium nitrate, and heated. When oxidation is complete, hydrochloric acid is added and the solution evaporated to a small bulk, diluted with water, filtered to remove siliceous matter, and the sulphate present estimated by precipitation with barium chloride.

Parkes and Major (*Analyst*, 1914, p. 160) have devised a 'glycyrrhizin test' which incidentally yields a colour reaction when senna is present.

The microscopical examination is important, for which a paper by Scott-Smith and Evans (*Analyst*, 1911, p. 198) proves useful.

A sample we examined proved to be simply powdered liquorice root as used for cattle. It contained 7·1 per cent. of ash, practically all of which was insoluble in water.

Grey Powder (*Hydrargyrum cum Creta*).—This consists of mercury mixed with twice its weight of prepared chalk. On treatment with dilute hydrochloric acid and removal of the mercury by filtration, the filtrate can be tested for mercuric salts with stannous chloride; mercuric salts should be absent. Tankard (*P.J.*, 1911, p. 72) found the powder to remain practically homogeneous for five months.

Seidlitz Powder. — Inaccuracy of weights is frequent failing. The blue paper should contai 7·5 grammes sodium potassium tartrate and 2· grammes sodium bicarbonate. The white pap should contain 2·5 grammes tartaric acid.

Sulphates of magnesium and sodium should b looked for as possible substitutes for sodium potassiu tartrate.

Solution of Hydrogen Peroxide.—For the assay *liquor hydrogenii peroxidi*, the following solution required, for which we give the *Codex* directions, thos of the B.P. being unintelligible to us. Five gramme of crystallised copper sulphate are dissolved in 80 c. of water, and ammonia solution is cautiously adde till the precipitate first formed is nearly dissolve It is filtered and the filtrate made up to 100 c. Two c.c. of the sample vigorously shaken with 4 c. of the copper ammonio-sulphate solution in a brine charged nitrometer should evolve not less than 18 c. nor more than 22 c.c. of oxygen. We have known 20-volume solution—*i.e.*, twice the B.P. strength— to be sold. Such a strong solution is used in the arts but to avoid possible accidents should be very dis tinctively labelled.

The B.P. limits acidity to 0·049 per cent. w/v calculated as sulphuric acid, and residue on evapora tion to 1 per cent. Barium salts are required to b absent.

This article does not keep well, and a preservative generally phosphoric acid, is added. Acetanilide i added for the purpose in one make.

Acetic Acid.—*Inter alia*, a test for formic acid i given in the B.P. Self (*P.J.*, 1915, p. 429) points ou that the neutralisation with ammonia as described i unnecessary, and if attempted even a small exces of ammonia will prevent a positive reaction.

Cream of Tartar.—Arising from the use of lea arsenate in the spraying of vines, acid potassiu tartrate frequently contains both lead and arsenic The Pharmacopœia gives a limit of 20 parts pe million for lead, which many samples reach, and on of 2 parts per million for arsenic, which is sometime exceeded.

Podophyllin.—The Pharmacopœia requires this to be soluble or almost entirely soluble in solution of ammonia, a requirement that is not always fulfilled by either the American or Indian drugs.

POISONOUS METALS IN FOODS.

The poisonous metals frequently occurring in foods are lead, tin, copper, arsenic, and zinc.

Lead may be found in drinking water, owing to contact with lead pipes, lead cisterns, etc. Soft waters and those with an acid reaction are peculiarly liable to this form of contamination. Aerated distilled waters readily dissolve lead, the excessive quantity of carbon dioxide forming lead bicarbonate, which is more soluble than the normal carbonate. The aerating apparatus is usually of block tin, which is very liable to contain lead as an impurity. The same with siphon heads; in France the amount of lead is restricted in these to 10 per cent., but even with 0·5 per cent. lead is given up to the water (Barillé, *Y.B.P.*, 1912, 369). In drinking-water or in aerated waters even traces (such as $\frac{1}{50}$ grain per gallon) are objectionable.

Lead is sometimes found in tinned foods, particularly in those containing free acid. Norway (1914) proposed a prohibition of tin-plate containing lead.

Tea, chocolate, and other foods wrapped in metallic foil may absorb the metal. Tea is often imported in chests lined with tin-foil containing lead. This is prohibited by France (1913) unless the tea is protected by the interposition of sheets of stout paper, aluminium, or fine tin.

Chrome yellow (lead chromate) has been used for colouring 'egg substitute' powders, confectionery, and pastry.

Cider and beer left standing in lead pipes are apt to take up lead, and it is also sometimes found in wine and beer brewed in glazed earthenware pans. Luff says that wine has been contaminated with lead, owing to shot used to clean the bottles being left in

them. Some wines are treated with litharge to remove acidity (Sainton).

Lead arsenate employed as an insecticide is present in the grapes at harvest, but is absent from the wine, probably owing to elimination with the skins and lees.

Red lead has been found in cayenne pepper, anchovies, and confectionery, and white lead in the ornaments used in adorning cakes. Lead is sometimes found in cream of tartar and other drugs.

Lead is a cumulative poison, and the continued introduction of minute quantities into the system produces a chronic state of poisoning

French Regulations (1910) prohibit the direct contact with sugar, glucose, honey, confectionery, preserves, jellies, marmalades, cocoa, chocolate, and liquorice, of tin containing more than $\frac{1}{2}$ per cent. of lead or more than 3 per cent. of any other metal.

Detection of Lead (and Copper).—Where the presence of organic matter prevents the direct application of tests, material may be dried (if necessary), moistened with strong pure sulphuric acid, and cautiously heated till completely carbonised. The ignition is continued till ash only is left. If the process is slow, the mass may be cooled and moistened with strong nitric acid from time to time. The ash is moistened with acetic acid, excess of ammonia and a little water added, and the liquid boiled and filtered. This is repeated till the ash is exhausted. The ammonia in a portion of the mixed filtrates is neutralised with hydrochloric acid, and a dilute solution of potassium ferrocyanide is added very cautiously. Any copper will produce a brown colour, and may be estimated colorimetrically, provided the relative proportions of the ferrocyanide solution are identical in both sample and standard. Excess of potassium ferrocyanide seriously diminishes the delicacy of the test.

In this process lead is converted into lead sulphate, which is soluble in ammonium acetate solution. To detect it, a further portion of the mixed filtrates is very faintly acidulated with hydrochloric acid and sulphuretted hydrogen passed through it, copper if present being kept in solution by the addition of

potassium cyanide. The colour of the lead sulphide may be matched against a standard lead solution (lead acetate, cryst., 0·183 gramme dissolved in a little water faintly acid with acetic acid, and made up to 1 litre: 1 c.c.=0·1 milligramme lead).

B.P. Quantitative Limit Test for Lead.—This test may be used for substances soluble in water, or in alkaline or acid solution. Twelve grammes of the sample are dissolved in hot water in a Nessler glass, filtered if necessary, rendered alkaline with ammonia, 1 c.c. of potassium cyanide solution (10 grammes in 100 c.c. of a solution containing 2 c.c. of H_2O_2) is added to keep copper from interfering, and the solution is made up to 50 c.c. This is the primary solution. Another Nessler glass containing 2 grammes of the sample is treated in the same way, and is called the auxiliary solution. If necessary, its colour is brought to the tint of the primary solution by the addition of a solution of burnt sugar.

To each cylinder is added 2 c.c. of sodium sulphide solution (10 per cent. w/v), and standard lead solution is added to the auxiliary glass till a tint equal to that of the primary solution is obtained. The quantity of standard lead solution represents the lead in the extra 10 grammes of the sample that is present in the primary solution.

Where the solubility of the sample is less, 7 or 4 grammes of it are used in the primary glass. For calcium hydrate and magnesium bicarbonate, acetic acid is used to effect solution.

The B.P. ignores the possible presence of iron, which would rank as lead, while the direction to filter is a device to be avoided where possible.

The results are calculated to parts per million, and the amounts permitted vary from 5 to 25 parts with different articles.

Detection of Lead in Water.—The sample should on no account be filtered, as this will remove a part, at any rate, of the lead. A water that has taken up lead in the ordinary course will nearly always be turbid, and the lead be present in suspension and not in solution. If any matter has settled out, the sample should be well mixed before taking any of it.

The most convenient plan is to place 100 c.c. of the sample in a Nessler glass 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). For further differentiation, advantage may be taken of the fact that sulphide of copper is soluble in potassium cyanide (giving a colourless solution) while sulphide of lead is not, but the test is better done in a solution that is not acid. The tint produced by sulphuretted hydrogen may be compared against a standard solution of lead acetate.

The presence of lead can be confirmed by the addition of a little solid potassium bichromate to a fresh portion of the water, when a turbidity is produced, best seen by holding the cylinder over a dark surface or a looking-glass.

The delicacy of both these methods is very considerable, and in each case it is possible to detect $\frac{1}{50}$ grain of lead per gallon.

The chromate method cannot be employed in liquids containing tartaric and other vegetable acids or organic matter, which have a reducing action on potassium bichromate.

Aerated water *not* supplied in siphons 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, their contents mixed in a jug, poured back into the bottles and sealed up.

Copper may be found as the colouring agent in preserved peas, French beans, spinach, pickles, and the mixed vegetables known as 'macédoines,' being added in the form of copper sulphate. The resultant green colour is due to an insoluble compound formed with chlorophyll—copper phyllocyanate. A considerable difference of opinion as to its toxicity exists. Luff says it is as detrimental as soluble copper salts, Schmidt found part of the copper was retained in the system, while Lehmann is of opinion that chronic poisoning by vegetables so preserved has probably never existed. Tschirch considers 0·1 gramme to be the largest amount of copper that can be taken daily

by a human being weighing 60 kilogrammes without danger. He considers a proportion of 1 part of copper in 20,000 as objectionable in view of the fact that with the ordinary diet the quantity of copper taken daily in the form of bread, meat, and vegetables amounts to about 1 milligramme. Should the phyllocyanic acid of the chlorophyll be insufficient to combine with the amount of copper added, the remainder forms copper leguminate. One member of the Departmental Committee dissented from the opinion expressed by the other members that such a substance as copper should be rigorously excluded. The dissentient, Professor Tunnicliffe, thought that the public would be sufficiently protected if the presence of copper were declared and did not exceed 0·07 part per 1,000 (0·5 of a grain per pound).

Provided its presence was notified, Canada (*Bull.* No. 366) tentatively allowed the use of copper with peas if it did not exceed 80 parts per million in the drained peas, nor more than 10 parts per million in the embedding liquid.

When present in preserved vegetables, copper is usually returned as 'equivalent to —'grains of crystallised sulphate of copper per pound.'

There is no evidence that potatoes absorb copper from plots treated with copper fungicide (Govt. Chemist). The copper found in tomatoes is said not to be affected in quantity by spraying with Bordeaux mixture, but it seems possible that the copper found in the soil in these experiments may have been due to spraying in former years. Copper may be found in tea that has been sprayed by Bordeaux mixture.

Copper is sometimes present in gelatin and always seems to occur in beer (up to 0·2 grain per gallon). It occurs naturally in the pigment of lobsters, in cocoa (up to 0·4 grain per pound), in peas, and in wheat. The quantity that has been found in oysters is considerably greater than in any other article of food.

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

The peas, beans, or pickles are carefully ignited till organic matter is burnt off. Plenty of sulphuric acid

should be employed during the charring, especially if a platinum dish is used, as otherwise the copper salts may be reduced to metallic copper, which will readily alloy with and penetrate a platinum dish, while it is, of course, well known that a fragment of lead or tin has the same effect.

A large quantity of the sample is ashed, the ash treated with sulphuric acid, diluted, filtered, made up to 40 c.c., and transferred to a platinum crucible capable of holding 70 c.c. The crucible stands on a piece of platinum foil connected to the 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 first with recently boiled distilled water, and then with spirit and ether, 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.

Another process is given under 'Lead.'

Arsenic is a frequent constituent of manufactured foods and drugs (see pp. 101 and 175). The Royal Commission on Arsenical Poisoning in their Final Report, 1903 (Cd. 1848) recommended that no substance used in food, whether intended for use alone or mixed with other substances, should contain more than $\frac{1}{100}$ grain of arsenic per pound if solid, or more than $\frac{1}{100}$ grain per gallon if beer, etc.

*Estimation of Arsenic.**—The Marsh-Berzelius method is employed for the detection and estimation of this impurity, and the hydrogen needed may be

* Arsenic in these estimations is always calculated to As_4O_6 (*vide* B.P., 1914, p. 501, par. 1, and Final Report of the Royal Commission on Arsenical Poisoning, Part I., 1903, p. 1, par. 3).

generated by the use of acid and zinc, or by an electrolytic method (*Analyst*, 1903, p. 349). In using acid and zinc errors may arise from the use of impure acid or zinc containing arsenic, or through the zinc being insensitive—*i.e.*, preventing the evolution of arseniuretted hydrogen when arsenic is present. It is therefore necessary to perform a blank experiment with the materials, and also to ascertain if the zinc is sensitive. The calcium chloride used in the drying-tube may also contain arsenic. An immense amount of work has been done to ascertain the best manner for the purification of materials, some papers to which reference may be made occurring in the *Analyst* (1903, pp. 3, 37, 101). A Joint Committee of the Society of Chemical Industry and of the Society of Public Analysts recommended the Marsh-Berzelius process, and described methods for obtaining pure materials (*Analyst*, 1902, p. 48). They found hydrochloric acid to be the most suitable acid, and recommended (*Analyst*, 1902, p. 210) that it be purified by adding to the strong commercial acid an excess of bromine and sulphurous acid, and then distilling, the first fifth of the distillate being rejected. Arsenic-free zinc can sometimes be obtained from dealers. The process is too long for insertion here, but it will be found in the *Analyst* (1902, p. 48). See also *Brit. Food Jour.*, 1902, pp. 170 and 191.

B.P. Quantitative Limit Test for Arsenic.—This test is that of Mayencon and Bergeret, and involves the production of a stain on mercuric chloride paper by arseniuretted hydrogen. It detects arsenic in both -ous and -ic combinations, and, while less sensitive than the Marsh-Berzelius test, does not require the frequent attention that the latter does.

The following reagents are required, all of which except the first must be practically arsenic-free: (*a*) Standard arsenic solution containing 0·00001 gramme of arsenious oxide in 1 c.c., prepared by diluting 1 c.c. of liquor arsenici hydrochloricus, B.P., to a litre; (*b*) zinc, to which the remarks made on its suitability for the Marsh test apply; (*c*) concentrated hydrochloric acid; (*d*) bromine solution, 30 grammes each of bromine and potassium bromide in 100 c.c.;

(*e*) stannous chloride solution, 20 grammes of tin partly dissolved in 60 c.c. of hydrochloric acid and made to 100 c.c. Sulphuric acid, calcium hydroxide, citric acid, and potassium chlorate reagents, may also be required.

A bottle of 120 c.c. capacity is fitted with a rubber stopper through the one hole of which passes a tube 2 decimetres long, a bore of 5 millimetres, the end entering the bottle being drawn out to a point having a bore of about 1 millimetre, and where the constriction commences—*i.e.*, still below the stopper—is a small hole. Through this hole the issuing gas passes into the tube, the 'pipette'-point being usually occupied with condensed moisture. The tube carries a piece of dry lead acetate paper, 4 by 10 centimetres, rolled up inside it, while its open (upper) end is capped with a dry bit of mercuric chloride paper kept in position by a rubber band.

The method of starting the test varies with different materials. As an example we give that prescribed for cream of tartar, as it requires no modification for baking and egg powders, the portion in brackets being that prescribed for glucose, which can be used without further modification for jams.

Five grammes of the sample and 50 c.c. of hot distilled water are placed in the bottle. Thirteen c.c. of hydrochloric acid containing 1 per cent. bromine solution (for glucose, add instead 0·5 c.c. bromine solution and 10 c.c. of pure hydrochloric acid) are added and left for five minutes. The colour of the bromine is discharged with a sufficiency of stannous chloride solution, 10 grammes of zinc are added, and the stopper already fitted with tube containing lead acetate paper and its outlet capped with mercuric chloride paper is inserted. The B.P. gives thirty to forty minutes for the completion of the reaction, which is usually sufficient, but the tests can quite well be left overnight. A yellow or orange stain, most obvious on the lower surface of the mercuric chloride paper, results if arsenic be present, and being proportional to its amount can be compared with stains produced under identical conditions by known amounts of the standard arsenic solution.

Where an article is unlikely to contain sulphides or sulphites, bromine need not be introduced, but stannous chloride is always added, as it assists in the production of a steady stream of hydrogen and reduces any -ic compounds to the arsenious state. Glycerin, alum, calcium chloride, calcium lactate, calcium phosphate, potassium bromide, potassium citrate, are all tested (in quantities of 2 to 5 grammes) with 50 c.c. of hot water and 10 to 14 c.c. of hydrochloric acid containing 1 per cent. of solution of stannous chloride.

Other gases besides arseniuretted hydrogen produce stains on the mercuric chloride paper. Hydrogen antimonide produces an orange or grey stain. Hydrogen phosphide and hydrogen sulphide produce yellow stains similar to the arsenical stain, and any sulphite in the bottle would be converted to hydrogen sulphide by the nascent hydrogen. The treatment with bromine removes most of the risk from sulphides, the little not oxidised being held back by the lead paper. All the same, a stain should always be cut out and immersed in concentrated hydrochloric acid. If due to sulphur compounds it will disappear in ten minutes, while an arsenical stain is greatly intensified—in fact, the use of hydrochloric acid on the stain adds to the delicacy of the test.

An arsenical stain fades rapidly (in an hour or two) in bright sunlight, but is practically permanent for several days in dull light. Dampness of the paper diminishes the intensity of the stain and access of ammonia to it turns it grey.

Some samples of zinc give too strong a current in a hot solution; this can be checked by placing the bottles in cold water. Contrariwise, if evolution of hydrogen is slack, it may be hastened by standing the bottles on top of a water-oven.

Standard stains require to be made at the same time as the sample is tested, the same amount giving stains of different intensity on different days.

A readier evolution of arseniuretted hydrogen is often obtained from the sample than from the standard. It is advisable sometimes to check standard

stains against samples in which the arsenic is estimated by the Marsh-Berzelius method.

The standard solution of arsenic does not keep and cannot be trusted if, say, a week old. Liquor arsenici hydrochloricus is stable.

Arsenic in foods and food-adjuncts is reported in grains per pound, in drugs in parts per million.

F. C. J. Bird (*Analyst*, 1901, p. 181) gives the following table for the identification of the stain:

	Appearance of Stain.	*Strong Hydrochloric Acid.*	
		Cold.	*Boiling.*
SH_2	Yellow to dull brown.	Stain dissolves slowly.	Stain dissolves immediately, leaving paper colourless.
PH_3	Yellow.	Bright lemon-yellow.	Somewhat intensified; bright lemon-yellow.
SbH_3	Brown-yellow to blackish-brown; fades on exposure to air.	Stain dissolves slowly.	Dissolves immediately; paper retains a grey tint.
AsH_3	Yellow to orange and orange-brown.	Stain intensified, full lemon-yellow to orange.	Stain further intensified; brick-red to deep red-brown.

Zinc is frequently found in dried apples, being derived from the galvanised wire on which the apples are dried. Its salts have been used in the manufacture of cheese (Allen and Hudson Cox, *Analyst*, 1897, p. 187), and the metal has been taken up by water passing through galvanised iron pipes. Some very hard waters act as readily as soft waters in this respect.

We have found zinc in tinned green plums, to which it had presumably been added as a colour fixative. It is usually present in ice-cream, and is taken up by milk from galvanised churns to a very slight extent while fresh, and to a much greater extent when sour. Owing to the ubiquity of gal-

vanised metal articles in food manufacture and preparation, traces of zinc occur in many of the staple foods.

Estimation of Zinc.—The material is extracted with dilute acetic acid, and the extract made ammoniacal. The residue is dried, thoroughly charred, and exhausted with very dilute hydrochloric or sulphuric acid; this is also made alkaline with ammonia and is added to the first extract. Through the mixed ammoniacal extracts, sulphuretted hydrogen is passed. The sulphides, etc., are filtered off, washed, and dissolved in water acidulated with sulphuric acid which is made up to a bulk of 50 c.c. in a Nessler cylinder. On the addition of a few drops of very dilute solution of potassium ferrocyanide a white cloud more or less slowly appears if zinc be present. The opacity of this cloud is measured against that produced by a standard solution of a zinc salt. It is of prime importance that precisely the same proportion of potassium ferrocyanide should obtain in both sample and standard mixtures, the zinc ferrocyanide being very susceptible to the reagent. Quite small traces of zinc may not come out and thus be missed if even a small excess of ferrocyanide be added.

Tin is found in varying quantities in canned articles, particularly in the case of acid fruits, such as cherries and currants, pineapples, pears, peaches, and apples.

Tinned tomatoes appear very liable to this form of contamination, especially when the fruit is allowed to stand in the opened tin—a condition which increases the risk of metallic poisoning with all these metals.

When a tin containing one or other of these acid fruits is opened it will be found invariably that the tin surface shows marks or etching. The more acid and the older the goods, the greater is the proportion of tin which leaves the vessel for the food. It is said that pineapples, etc., are imported in tins and transferred to glass vessels in this country for sale; this to delude the public into a sense of security.

In canned foods the tin may exist in soluble, insoluble, or colloidal forms. W. D. Bigelow (*Analyst*, 1916, p. 342) says the longer the food has been canned, the higher is the proportion of insoluble tin,

tin originally in solution being slowly rendered insoluble.

Some tins of beef essence sent out to Africa during the war, and subsequently returned to this country, were examined, and found to contain tin up to 22 grains per pound (see Report of L.G.B. on 'The Changes in Certain Meat Essences kept in Tins for Several Years,' 1906).

Tin is estimated by Schryver's process (1908, *Repts. Insprs. Foods, L.G.B.*, No. 7). The organic matter is destroyed with sulphuric acid and potassium sulphate as in the Kjeldahl-Gunning process (p. 31), and the tin is either precipitated as sulphide, purified and weighed as oxide, or else it is estimated colorimetrically with dinitrodiphenylamine sulphoxide. Buchanan and Schryver (*loc. cit.*) regard canned food containing quantities of tin approximating to 2 grains to the pound with suspicion, as liable to produce irritant action.

Sampling.—After opening the sample, the *whole contents* should be pulped or mixed, and the estimation should be done on a portion of this mixture. This procedure was discussed (*Analyst*, xxii., p. 145), as some analysts are in favour of separating the liquid and solid portions of the sample before examination. In the case, however, of canned cherries, currants, etc., it is probable that any heavy metals would be mainly in the liquid, and an additional reason for examining the syrup would be that many people would use it for food together with the fruit.

In the case of nearly all canned articles, it is possible, by using a very moderate amount of violence, to detach small beads of solder from the inside of the tin. Such fragments should be searched for and removed, as it would be obviously unfair to dissolve and estimate them along with any metal actually in chemical combination, and a small fragment of solder in, say, 10 or 20 grammes of sample would show a very much higher figure than is ever likely to be obtained from metal really in a state of combination with the sample. As an illustration, if two No. 5 shot were contained in a snipe, and were ingested together with the flesh of that bird, the lead would

bear the proportion to the flesh of about 20 grains to the pound—a quantity that would rightly be condemned if in combination, but which in the metallic state is probably harmless.

COMMERCIAL DISINFECTANTS.

Information on the varieties of disinfectants, their uses and valuation, will be found in 'Aids to Bacteriology.'

Assay of Carbolic Powders.—Either 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 c.c. of 10 per cent. solution of caustic potash or soda, and the spirit distilled off and the liquid evaporated to about 30 c.c. 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 neutralised. 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 cubic centimetres thus obtained by 1·05 and then 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:

Fifty grammes of the carefully sampled powder are placed in a large mortar, and a cold mixture of equal parts of 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 volatilisation. If the operation has been well conducted, the powder will when neutralised 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 c.c. 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 c.c., transferred to a burette, and treated as described above.

Liquid Carbolic Preparations.—Several liquid preparations depend for efficacy chiefly on the amounts of carbolic and cresylic acids they contain. Some 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 distilling and extracting the phenols from the distillate in the ordinary way. As the acid is seldom or never in combination, throwing up the tar acids with 20 per cent. sulphuric acid previous to distillation is unnecessary.

SOAP.

Hard soaps are made of various animal and vegetable oils and fats saponified with caustic soda. Low-grade soft soaps are manufactured from fish and other low-grade oils, potash being used in the saponification. The better class of soft soaps are made from the finest oils, such as olive oil, cotton-seed oil, and tallow. One hundred parts of neutral glyceride produce about 150 parts of finished soda soap.

Resin is a legitimate substitute (partial) for fatty matter in the common soap used for household and manufacturing purposes, as the resinates possess powerful detergent properties. To a certain extent it masks the odour due to putrid fats, and resin soaps are liable to leave a sticky feeling on the skin after use. It is said to be used in the manufacture of transparent soaps, as it allows the production of a considerable transparency. Glucose is used for making transparent soaps, but, generally speaking, they are chiefly clarified by dissolving the original soap in an alcoholic solution, and the alcohol is then recovered by distillation.

Soap-powders, washing-powders, dry soaps, etc., are generally mixtures of carbonate of soda with dried and powdered soap, sometimes with the addition of sodium sulphate and other inert materials. A fine silica is mixed with soap in some soap-powders.

The Analysis of Soap.

Water.—A known weight of the soap is dissolved in water, and the solution made up to a definite volume. A measured portion is absorbed by sand or gypsum and then gradually and completely dried at from 100° to 105° C.

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

The Pharmacopœia directs the drying to be done at 110° C. and imposes limits of 30 per cent. for moisture in both curd and hard soaps.

Uncombined Fat.—Ten grammes, after drying, are exhausted with petroleum ether, which dissolves any unsaponified fatty matter, hydrocarbon 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 c.c. of hot neutral alcohol until all that will is dissolved. The alcoholic solution is then filtered, and the filter washed with neutral alcohol. The filtrate is then made up to a definite volume, and divided into two equal parts—*a* and *b*.

(*a*) To this solution (=5 grammes of the original sample) are added one or two drops of solution of phenolphthalein, 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*.

The Pharmacopœia requires curd, hard, and soft soaps to yield no free alkali hydroxide. (By stipulating that the alcoholic extract should be neutral in the case of curd soap, the Pharmacopœia requires absence of free fatty acids.) It omits preliminary extraction with petroleum ether from its process.

(*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 alkalis; 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.

The Pharmacopœia requires curd and hard soaps not to exceed limits of 0·53 per cent. of alkali carbonates calculated as anhydrous sodium carbonate, and soft soap not to exceed 0·69 per cent. calculated as anhydrous potassium carbonate. Self (*P.J.*, 1915, p. 419) criticises the extraction with 90 per cent. alcohol as it is directed to be used in the Pharmacopœia, on the ground that it will almost certainly dissolve out some carbonate.

Fatty and Resin Acids.—Five grammes of the soap are dissolved in hot water (cooled and exhausted with ether if free glycerides or unsaponifiable matter is present), the aqueous solution is then acidified with dilute sulphuric acid, and the whole is boiled up until the *fatty acids are perfectly clear*. The free 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.

Instead of removing with ether, the fatty acids may be put on a wet filter and washed with distilled water till free from mineral acid.

The Pharmacopœia requires the fatty acids from hard and soft soaps to possess the following characters: Melting-point, 21° to 28° C.; refractive index at 40° C., 1·454 to 1·458; iodine value, 83 to 92; acid value, 195 to 205. These are both olive-oil soaps. Curd soap is made from animal fats.

Butcher's fats usually give a 'titer' (melting-point of fatty acids) of 43° C., and produce a hard soap. Fats and oils with a lower titer give softer soaps. A titer value of 40° C. is often stipulated in making contracts for soap. This requirement keeps out a lot of, but not all, rubbish. It also excludes coconut oil (24° C.).

Resin.—The resin is estimated in the fatty acids by the method devised by Twitchell (*Analyst*, 1891, p. 169). 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.—Lewkowitsch has found the following method sufficiently accurate for all practical purposes: 50 grammes of the sample are dissolved in water, and about 20 c.c. 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). More salt is added if necessary, then acidified 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 ..	0·1	0·2	0·3	0·4	0·3	2·1	3·2
Silica	0·3	0·8	none	0·2	none	7·0	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

COEFFICIENTS 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
$Ca(HO)_2$	·037
CaO	·028
$CaCO_3$	·05
$Ba(HO)_2$	·0855
$Ba(HO)_2 8H_2O$	·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
K_2O	·047

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

Normal Soda Solution (*continued*)

H_2SO_4	·049
$H_2C_4H_4O_6$ (tartaric)	·075
$HC_3H_5O_3$ (lactic)	·09
$H_2C_2O_42H_2O$ (oxalic)	·063
H_3BO_3 (boric)	·062
Oleic	·282
Malic	·067

$\frac{N}{10}$ 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
KI	·0166

$\frac{N}{10}$ 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

$\frac{N}{10}$ 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
$H_2C_2O_42H_2O$ . . .	·0063
$CeC_2O_4.9H_2O$ . . .	·354

Nitrometer Analysis.

Each c.c. 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 c.c. of CO_2 at N.T.P. equals gramme of	·0042	$(NH_4)_2CO_3$
	·001967	CO_2

USEFUL DATA.

To convert—	*Multiply by—*
Ounces to grammes	28·349
Grains to grammes	·0648
Grammes to grains	15·432
Pints to cubic centimetres	567·936
Gallons to litres	4·548
Litres to gallons	·22
Kilogrammes to pounds	2·2046
Centimetres to inches	·3937
Inches to centimetres	2·54
Grammes per 100 cubic centimetres to grains per fluid ounce	4·375
Grammes per 100 cubic centimetres to grains per gallon	700
Parts per 1,000,000 into grains per gallon	·07
Grammes per 100 grammes to grains per pound	70

APPENDIX

ALTERATIONS IN THE COMPOSITION OF FOOD AND DRUGS DUE TO WAR.

To the best of our information, the following include all Orders having the effect of law that bear on the subject-matter of this book, issued to March 7, 1918.

Defence of the Realm (Liquor Control).

General Order (Amending) of the Central Control Board (Liquor Traffic).—Whisky, brandy, rum, and gin, must be reduced to 25° under proof. Adulteration by admixture with water is not recognised till the spirit has been reduced to more than 50° under proof.

Alterations in the 1914 British Pharmacopœia.

The General Medical Council has withdrawn from the Pharmacopœia the medicines and compounds, and the directions for preparing them, set forth in the following schedule, until legal order respecting them is made:

All confectiones, *except* confectio piperis, confectio rosæ gallicæ.

All glycerina, *except* glycerinum.

All misturæ, *except* mistura cretæ, mistura ferri composita, mistura olei ricini.

All syrupi, *except* syrupus, syrupus chloral, syrupus codeinæ phosphatis, syrupus ferri iodidi, syrupus ferri phosphatis cum quinina et strychnina, syrupus glucosi.

All trochisci, *except* trochiscus krameriæ et cocainæ, trochiscus morphinæ, trochiscus morphinæ et ipecacuanhæ.

Also caffeinæ citras effervescens, decoctum aloes compositum, extractum gossypii radicis corticis liquidum, linimentum potassii iodidi cum sapone, liquor calcis

saccharatus, magnesii sulphas effervescens, mel boracis, pulvis amygdalæ compositus, pulvis glycyrrhizæ compositus, pulvis tragacanthæ compositus, sodii citrotartras effervescens, suppositoria glycerini, tinctura cardamomi composita, tinctura kino, tinctura pruni virginianæ, tinctura rhei composita, tinctura sennæ composita, unguentum iodi.

Alternative formulæ eliminating glycerin and sugar are published in an Addendum to the British Pharmaceutical Codex.

Gum tragacanth in chloroform water is recommended for attaining the taste and consistence of a syrup.

Ministry of Food Orders.

Those Orders marked with an asterisk have been superseded by others at the time the proof was corrected.

The Manufacture of Flour and Bread Order, 1917.—The existing requirements of the Bread Acts of 1822 and 1836 for the marking of loaves with an M. to indicate that they are mixed are abrogated during the continuance of this Order.

Manufacture of Flour and Bread Order (No. 2), 1917, makes it compulsory on all millers to extract from the wheat not less than 81 per cent. of flour. (At the time of writing, a requirement of 95 per cent. extraction is said to be under consideration.)

Manufacture of Flour and Bread Order (No. 2), 1917 (Directions relating to Imported Flour) (No. 1219).—Except in Scotland, where it must not exceed 50 per cent. (wholesale manufacture of biscuits not included), imported flour must not exceed 25 per cent. of any flour sold by retail or used for any purpose. The idea underlying this order is that imported flour would not conform to the 81 per cent. regulation.

The Manufacture of Flour and Bread Order (No. 3), 1917 (No. 315).—This Order increases the percentage of flour from other cereals to be mixed with wheaten flour, from a maximum of 15 per cent. to a maximum of 25 per cent., and from a minimum of 5 per cent. to a minimum of 10 per cent.

The catalogue of materials allowed to be mixed is carried on from the No. 2 Order, which permitted rice,

barley, maize, semolina, oats, rye, or beans. Mixtures must be made by the millers before selling their flour. (See below for use of potatoes.)

The Cake and Pastry Order, 1917 (No. 372), *inter alia*, provides that sugar shall not exceed 15 per cent. and wheaten flour shall not exceed 30 per cent. in cake; that sugar shall not exceed 10 per cent. and wheaten flour shall not exceed 50 per cent. in a bun; that a scone must contain no sugar nor more than 50 per cent. of wheaten flour; and that no biscuit shall contain more than 15 per cent. of sugar.

'Wheaten flour' is defined as 'any flour for the time being authorised to be used in the manufacture of wheaten bread,' and 'sugar' includes glucose. The original Order directs 'all sugar contained in the baked article shall be taken into account, in whatsoever form it may have been introduced.' In the process used for the determination of sugar (see *Analyst*, September, 1917), an allowance of 3 per cent. for sugars natural to flour or formed in baking, and another of 2 per cent. for variations in sampling and experimental errors, are sanctioned. Also any sugar derived from added fruit does not count.

The Bread Order, 1917, provided, *inter alia*, that no currant, sultana, or milk bread may be sold; and that no sugar may be used in making bread.

***The Margarine (Maximum Prices) Order, 1917 (No. 1162)**, permits oleo-margarine to be sold at a higher price than other margarine. 'Oleo-margarine' is defined as containing not less than 55 per cent. of specified animal fats, but excludes hardened oils.

The Milk (Use in Chocolate) Order (No. 2), 1917 (No. 1296).—An Order forbidding the use in the manufacture of chocolate, of milk, condensed milk, milk powder, dried milk, or any other milk preparation.

The Sugar (Brewers' Restriction) Order, 1917.—This Order prohibits the use by brewers of any saccharine substance other than solid glucose or the invert or other produce of low-grade cane-sugar polarising not over 89°, and from which not less than 40 per cent. of its weight has already been extracted in the form of grocery crystal sugar, honey sugar, or syrup.

***The Beer (Prices and Description) Order, 1917 (No. 1058)**.—When sold in a public bar, the maximum price

for beer of an original gravity less than 1,036° shall be at the rate of 4d. per imperial pint, and for beer of an original gravity not exceeding 1,042° and not less than 1,036° shall be at the rate of 5d. per imperial pint.

A Public Analyst's certificate under this Order is accepted as *primâ facie* evidence.

*(The Secretary to the Ministry of Munitions stated in Parliament August 20, 1917, that the only condition affecting the quality of 'Government ale' is that it must not exceed a gravity of 1,036°.)

The Milk (Amendment) Order (No. 1317), *inter alia*, prohibits the addition of colouring matter or water to milk. It does not apply to milk sold for consumption on the premises of the seller.

The Bread (Use of Potatoes) Order, 1918 (No. 14), permits the use in the manufacture of bread of such quantities of potatoes as the maker may think fit.

The Jam (Prices) Order, 1918 (No. 68), requires any scheduled jam or jelly to comply with the following provisions: (*a*) Not more than 10 per cent. measured by weight shall consist of added fruit juice; (*b*) when more than one fruit is mentioned in the description, it must amount to not less than 25 per cent. by weight of the total fruit; (*c*) the dried weight of the ingredients must be not less than 65 per cent. of the total weight.

Marmalade, or any article of which the word 'marmalade' forms part of the description, must be made solely from citrous fruits, citrous fruit juices, sugar or other sweetening substances and preservatives.

Articles sold for consumption on the premises or in quantities of less than 4 ounces are exempt.

Sausages for purposes of local meat rations are divided into first and second qualities containing, respectively, not less than 67 and 50 per cent. of butcher's meat (including pork) or offal (*National Food Journal*, February 13, 1918).

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