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Obituary

WILLIAM FOULKES LOWE

IT is with great regret that the death of W. Foulkes Lowe is recorded.

Lowe was an old member of the Society, having been elected in 1888. He served on the Council during the years 1902 and 1903, but his activities in this and in many other ways were restricted by his deafness; yet, the furtherance of the influence of the Society was ever his desire and aim.

Born in 1849 of an old Chester family, he received his education at the King's School, Chester, which then held its classes in the refectory of the Cathedral. He was subsequently a student at the Royal School of Mines, London, and at the Owens College, Manchester, and later became an Associate of the Royal School of Mines and a Fellow of the Institute of Chemistry.

In 1871 he was made a member of the Goldsmiths' Company, and in 1876 was appointed Assayer of the Chester Assay Office, subsequently becoming Assay Master. The Chester Goldsmiths' Company was incorporated in 1700.

To the Society, Lowe was best known as a Public Analyst, and it is of interest to note that he received his first appointment, that of the City of Chester, in 1876. Other appointments as Public Analyst which he held at his death were for the County of Flint (1878), the County of Carnarvon (1881), and the Counties of Anglesey and Denbigh. In addition, he held the position of Official Agricultural Analyst of these counties. A considerable general private practice included the assaying of a large number of gold, lead and zinc ores.

In common with many other Public Analysts, Lowe in his early years lectured, and demonstrated at chemistry lectures (at both Chester and Wrexham) under the old South Kensington Scheme. For many years he was a keen supporter of the Chester Society of Natural Science, Literature and Art, and I well recall some of his early lectures which invariably drew a large audience, no doubt attracted, in part, by the many experiments he would carry out on these occasions. Several years ago the Chester Society awarded him the Kingsley Medal in recognition of his work.

Considering his ability and his extraordinarily wide knowledge, Lowe leaves behind an unexpectedly small amount of published literature. His chief

contributions appeared in the *Journal of the Society of Chemical Industry*, *The Chemical News* and THE ANALYST. His early papers usually referred to the assaying of gold, lead or zinc, but "The Facing of Rice," "Dirt in Milk," "The Occurrence of Copper in Oysters," and "The Adulteration of Spirits of Nitre," are among more recent papers contributed to journals.

Much of his spare time was spent on the water, for he was a keen oarsman, and few had a greater knowledge of sailing. For many years he was a member of the Chester Rowing Club and of the Dee Sailing Club.

He is survived by his widow and three sons, one of whom—Harold Lowe—continues his father's practice, and is a member of our Society, and Public Analyst for Shropshire and elsewhere.

Long will his kindliness live in the hearts of all his colleagues and others who knew him.

F. W. F. ARNAUD.

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

XXI. A Reliable Method for the Quantitative Separation of Titanium from Tantalum and Niobium

BY W. R. SCHOELLER, PH.D., AND C. JAHN

(*Work done under the Analytical Investigation Scheme*)

(*Read at the Meeting, November 4th,* 1931)

A PROVISIONAL method for the separation of small amounts of earth acid from titania was described in Section XIV (ANALYST, 1929, **54**, 320). Since then we have continued our researches, and have succeeded in elaborating the perfected method recorded below. It is of general applicability to mixtures of earth acid and titania in any proportions; and, as the results obtained by it are reasonably accurate, it brings to a successful conclusion our study (begun by the senior author in 1923) of what was once considered to be a problem of almost insuperable difficulty in mineral analysis.

RATIONALE OF THE METHOD.—It may be recalled that the separation in question has been discussed in three earlier Sections: IX (ANALYST, 1927, **52**, 633); XIV (*loc. cit.*); and XV (*id.*, 1929, **54**, 453). In each paper a new method for carrying out the separation was indicated: (*A*) Precipitation of the earth acids from the tartrate solution by excess of mineral acid ("tartaric hydrolysis"); (*B*) precipitation of the earth acids by calcium chloride from the oxalate solution containing sodium salicylate ("oxalate salicylate method"); and (*C*) extraction of the bisulphate melt of the mixed oxides with acid tannin solution, the earth acids remaining in the residue ("pyrosulphate tannin method").

We may say at once that continued investigation established the superiority of method *B* over its rivals; hence its principle was made the basis of the new general process. At the same time, the other two methods proved most useful—indeed indispensable—auxiliaries. Method *C* is actually used in our new process for the recovery of the minor earth-acid fraction. As for Method *A*, its great value lies in the specificity of the precipitation reaction as well as in its quantitative applications (*vide* XV, *loc. cit.*, p. 456; XIV, *loc. cit.*, p. 321).

Synopsis.—The first step in the present method (precipitation of the major earth-acid fraction) remains the same as in XIV (*loc. cit.*). Briefly, we produce the calcium oxalate precipitate containing the earth acids, destroy the oxalic acid in the precipitate by means of permanganate in hydrochloric acid solution, and precipitate the earth acids with tannin as heretofore; this furnishes the major fraction P^1. The yellow salicylate filtrate from the oxalate precipitate, however, is now precipitated with tannin and ammonium acetate (*cf.* XVII, ANALYST, 1929, **54**, 709); the ignited precipitate, P^{1a}, represents the titania fraction, which carries a small balance of earth acids. These are recovered from P^{1a} by fusion with bisulphate and application of method *C* as a small precipitate Π^1, which is added to P^1. The sum $(P^1 + P^{1a})$ gives the total amount recovered, $(P^1 + \Pi^1)$ the earth acid recovered.

PRELIMINARY TESTS.—The following results were obtained in a series of exploratory analyses. It should be stated that the earth acids are not precipitated as such with the calcium oxalate, but as bulky salicylic acid complexes, that of tantalum being white, and that of the niobium compound yellow. Exps. 1 and 2, in which no titania was added, show that several mgrms. of earth acid escape precipitation at the P^1 stage:

Exp. 1.	Taken, M_2O_5	0·1010 grm.	P^1:	0·0972 grm.
„ 2.	„ Nb_2O_5	0·1814 „	P^1:	0·1759 „

The table below gives four test separations of niobic oxide and two of tantalic oxide from titania:

Exp.	M_2O_5 taken. Grm.	TiO_2 taken. Grm.	P^1. Grm.	P^{1a}. Grm.	Π^1. Grm.	TiO_2 in $(P^1+\Pi^1)$* Grm.	M_2O_5 in $(P^1+\Pi^1)$† Grm.	M_2O_5 error. Grm.	Total recovery error. Grm.
Nb 3	0·1814	0·0241	0·1805	0·0248	0·0021	0·0026	0·1800	−0·0014	−0·0002
„ 4	0·1814	0·0234	0·1801	0·0234	0·0030	0·0037	0·1794	−0·0020	−0·0013
„ 5	0·2027	0·0246	0·1971	0·0274	0·0038	0·0021	0·1988	−0·0039	−0·0028
„ 6	0·1491	0·0249	0·1476	0·0247	0·0028	0·0019	0·1485	−0·0006	−0·0017
Ta 7	0·1554	0·0122	0·1536	0·0120	0·0015	0·0007	0·1544	−0·0010	−0·0020
„ 8	0·1758	0·0254	0·1779	0·0212	0·0027	0·0049	0·1757	−0·0001	−0·0021

* By colorimetry. † By difference.

The figures prove that 90 per cent. (more or less) of the titania has been eliminated at the cost of a certain loss in earth acid. Re-treatment of $(P^1 + \Pi^1)$ by the same method suggested itself as the means for completing the separation; the products of such re-treatment being P^2, P^{2a}, and Π^2, the titania content of the combined earth-acid fractions $(P^2 + \Pi^2)$ in our final experiments fell below 0·001 grm. Although, therefore, total elimination of the titania from the earth-acid fraction was not achieved, we are quite satisfied with the efficacy of the separation, since all we require is an earth-acid fraction sufficiently low in

titania to admit of a satisfactory separation into tantalic and niobic oxides, as specified in Section XI (ANALYST, 1928, **53**, 266). The minute amount of residual titania in the pentoxides is, of course, determinable by colorimetry.

Turning our attention to the negative recovery errors observed in the preliminary tests, we located practically the whole of the missing oxides in the filtrate from the tannin precipitate, P^1. This filtrate still contains a fair excess of hydrochloric acid, and, by neutralisation, followed by addition of tannin and excess of ammonium acetate, we obtain a few mgrms. of precipitate, p^1, which is added to P^{1a}.

As a precautionary measure we also re-work the salicylate filtrate from P^{1a}, by simply boiling it down and leaving it overnight. It sometimes yields a fraction of a mgrm. of titania as a small precipitate, p^{1a}, which also is added to P^{1a} before this is worked up for Π^1.

The same manipulations are carried out during the second stage of the separation: the small precipitates, p^2 and p^{2a}, are combined with P^{2a} and converted into Π^2.

The accuracy of the method in its final form does not leave much to be desired, as shown by the results of the test separations (*vide infra*).

PYROSULPHATE TANNIN METHOD FOR SMALL QUANTITIES OF EARTH ACID:—Before describing the improved oxalate salicylate method, we must give certain data on the recovery of the minor earth-acid fraction from the titania fraction (large or small) by means of the pyrosulphate tannin method, which constitutes an important step in the present process.

Procedure.—This is described in XV (*loc. cit.*, p. 455, first paragraph). In this case the precipitate TP, being small, should be left to stand for several hours in the cold (after the liquid containing it has been heated to incipient boiling), prior to filtration, or overnight, if convenient. A 150 c.c. beaker is more suitable than a 400 c.c. one for the quantities involved.

If the proportion of titania in the mixed oxides is high, TP may be re-treated after ignition by the same method, yielding TP^2. The residual titania in TP or TP^2 is determined colorimetrically, M_2O_5 being obtained by difference. (For a specific earth-acid test in TP, see XV, *loc. cit.*, p. 455.)

Results of Test Separations.—The table below shows the results of eight tests on small amounts of mixed pentoxides with increasing additions of titania. Re-treatment of TP was carried out in Exps. 14 to 16; the titania content given in Column 6 was determined colorimetrically in TP or TP^2, the M_2O_5 in Column 7 being taken by difference:

Exp.	M_2O_5. Taken. Grm.	TiO_2. Added. Grm.	TP. Grm.	TP^2. Grm.	TiO_2 in TP. Grm.	M_2O_5 in TP. Grm.	M_2O_5. Error. Grm.
9	0·0061	none	0·0060	—	—	0·0060	−0·0001
10	0·0039	0·0100	0·0041	—	0·0004	0·0037	−0·0002
11	0·0044	0·0200	0·0050	—	0·0008	0·0042	−0·0002
12	0·0046	0·0420	0·0062	—	0·0019	0·0043	−0·0003
13	0·0073	0·0606	0·0092	—	0·0022	0·0070	−0·0003
					in TP^2	in TP^2	
14	0·0055	0·1012	0·0087	0·0052	0·0001	0·0051	−0·0004
15	0·0078	0·1502	0·0149	0·0068	0·0003	0·0065	−0·0013
16	0·0058	0·2034	0·0145	0·0053	0·0003	0·0050	−0·0008

With the exception of the abnormal result in Exp. 15, the recovery of the few mgrms. of earth acid admixed with excess of titania must be considered very satisfactory, especially when it is borne in mind that, until quite recently, even the qualitative recognition of earth acid in such mixtures was very uncertain. The recovery being slightly incomplete, it follows that the negative error increases as the result of the re-treatment of *TP*. For this reason the operator will generally find it preferable, when applying the oxalate salicylate method, to confine himself to a single pyrosulphate tannin treatment of the minor earth-acid fraction; the earth-acid loss will thus be kept at a minimum, while the higher titania content of the fraction is adequately removed in the second salicylate treatment.

Whilst the oxalate salicylate method is the most accurate process for the separation of the earth acids from titania in general, we have in the pyrosulphate tannin method an extremely simple procedure for tracing very small quantities of earth acid in titania.

THE OXALATE SALICYLATE METHOD.—The mixed oxides (about 0·25 grm.) are brought into solution by fusion with potassium bisulphate (3 grms.) in a silica crucible and treatment of the mass with a hot, strong solution of ammonium oxalate (2·0 grms.) in an 800 c.c. beaker. Five grms. of sodium salicylate B.P., dissolved in hot water are added to the boiling solution (bulk, 250 c.c.), which is stirred and precipitated with a slight excess of 20 per cent. calcium chloride solution, added gradually in small portions. The solution must not be allowed to cool; after a few minutes' settling on the water-bath, the supernatant liquid is tested for complete precipitation with a little calcium chloride, and filtered at once by suction on an 11 cm. No. 40 Whatman filter supported by a platinum cone. The precipitate is washed with a hot 2 per cent. sodium salicylate solution until the washings are colourless. The yellow filtrate and washings are transferred to another 800 c.c. beaker and heated to boiling (see *a*).

Major Earth-acid Fraction, P^1.—The oxalate precipitate is returned to the precipitation vessel, the filter being spread against the side of the beaker; the paper is washed with hot water, followed by 40 to 50 c.c. of hydrochloric acid (1:1), and again with water, then ignited, and the ash added to the solution. This is heated and cautiously treated with excess of strong permanganate solution. When the transient brown colour of the higher manganese compounds has been discharged by further boiling (and addition of a few drops of tannin solution if required), the liquid is diluted to 300 c.c. with boiling water, treated with 1 grm. of tannin (fresh, strong solution), boiled for 5 to 10 minutes, and the precipitate P^1 is left to settle for some hours. It is mixed with filter pulp, filtered off under gentle suction, washed with 2 per cent. ammonium chloride solution containing a little tannin, and ignited wet in a porcelain crucible.

Intermediate Fractions p^1, P^{1a}, p^{1a}.—(1) The filtrate from P^1 is neutralised with ammonia (1:1), treated with 5 c.c. of acetic acid and 10 grms. of ammonium acetate, boiled down to 300 c.c., and another 0·5 grm. of tannin added. After settling overnight, the small precipitate, p^1, is collected and washed in the same way as P^1.

(2) The boiling yellow filtrate (*a*) (*supra*) is treated with 10 grms., each, of

ammonium acetate and chloride, and 1 to 2·5 grms. of tannin (about 12 times the weight of the titania) in fresh, strong solution. The voluminous red precipitate is left to settle on the water-bath, and filtered off under gentle suction on a 12·5 cm. filter for quantities up to 0·15 grm.; with larger amounts the precipitate is divided between two filters. After being washed in the same way as P^1, the precipitate P^{1a} is ignited in a silica crucible, together with p^1.

(3) The filtrate and washings from P^{1a} are boiled down to about 250 c.c., 0·5 grm. of tannin being added towards the end, and the liquid left overnight. It is then filtered, and the very small dark precipitate, p^{1a}, washed as before and added to the silica crucible containing P^{1a} and p^1.

Minor Earth-acid Fraction, Π^1.—The ignited intermediate precipitates are fused with potassium bisulphate (1 to 3 grms.), and the cold fusion product is extracted with a 1 per cent. solution of tannin in 5 per cent. sulphuric acid. The hot reagent is poured into the crucible, which is gently heated with a moving bare flame. The contents of the crucible are transferred to a 150 c.c. beaker, and the crucible is rinsed with the reagent (25 to 80 c.c.). The liquid is heated to boiling, then left in the cold for some hours or overnight. The precipitate, Π^1, is collected, washed with 5 per cent. sulphuric acid, ignited, and added to P^1. The filtrate from Π^1, containing the major titania fraction, is reserved if the titania has to be determined.

Re-treatment of $(P^1 + \Pi^1)$.—The united precipitates are once more subjected to the whole process so far described. After bisulphate fusion and solution of the product in ammonium oxalate solution, the liquid is filtered if necessary, any residue being ignited and treated with hydrofluoric acid and a drop of sulphuric acid in a small platinum cup; the residue is fused with a speck of bisulphate, taken up with 2 to 3 c.c. of ammonium oxalate solution, and added to the bulk.

The re-treatment yields a major earth-acid fraction, P^2, and the small intermediate fractions p^2, P^{2a}, and p^{2a}; these are combined and worked up by the pyrosulphate tannin method for Π^2, the minor earth-acid fraction, the filtrate from which is combined with that from Π^1. The final products of the operation are: (1) $(P^2+\Pi^2)$, which is weighed as $(Ta,Nb)_2O_5$; if bulky, its weight should be checked after lixiviation and another ignition (XIX, ANALYST, 1931, **56**, 309); and (2) the combined filtrate from Π^1 and Π^2.

Determination of Tantalum and Niobium.—The weighed precipitate $(P^2+\Pi^2)$ is fused with bisulphate, the mass dissolved in ammonium oxalate solution, and the earth acids separated from each other by Powell and Schoeller's process (IV, ANALYST, 1925, **50**, 489).

Direct Determination of the Titania.—The titania may be taken by difference, the weight of $(P^2 + \Pi^2)$ being subtracted from that of the mixed oxides taken. The direct determination may be useful as a check where the quantity of titania is small, though as the titania is a final product, it need not be subjected to further manipulation. For its recovery, we have the choice of two procedures: (1) With smaller amounts of titania, the combined filtrate from Π^1 and Π^2 is diluted, nearly neutralised with ammonia, boiled, and treated with a large excess of ammonium acetate and nitrate. The precipitate is washed with ammonium chloride solution containing a little tannin, ignited, purified by leaching, ignited and weighed; an allowance for iron may have to be made. (2) For large quantities, the combined

filtrate is treated for the destruction of the tannin (XIX, *loc. cit.*, 306). The titania in the residual sulphate liquor is determined by thiosulphate hydrolysis.

RESULTS OF TEST SEPARATIONS.—The table below gives the results of a series of six consecutive test separations of mixtures, the composition of which was unknown to the operator. Three contained niobic pentoxide, two tantalic pentoxide, and the last, the mixed pentoxides (see Column 1). In Exps. 17 to 19, pentoxide preponderated over titania; in 20 and 21, titania was the main constituent; in 22, the ratio of pentoxide to titania was about 1:1.

Exp.	M_2O_5. Taken.	TiO_2. Taken.	TiO_2. Recovered.	P^1.	P^2 leached.	Π^2.	$P^2+\Pi^2$.	M_2O_5. Error.	TiO_2 in $(P^2+\Pi^2)$.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
Ta 17	0·2023	0·0516	0·0508	0·2036	0·1937	0·0078	0·2015	−0·0008	0·0008
Nb 18	0·2027	0·0513	0·0512	0·2025	0·1954	0·0049	0·2003	−0·0024	0·0006
Nb 19	0·1965	0·0535	0·0531	0·1963	0·1890	0·0053	0·1943	−0·0022	0·00075
Ta 20	0·0335	0·2010	0·1986	0·0314	0·0266	0·0073	0·0339	+0·0004	0·0003
Nb 21	0·0439	0·2067	0·2068	0·0424	0·0368	0·0071	0·0439	0·0000	0·0007
EA 22	0·1257	0·1176	0·1173	0·1273	0·1225	0·0033	0·1258	+0·0001	0·0009

The accuracy of the method will now be considered in the light of the above results. The titania recovery may be dismissed with the remark that it is satisfactory, with the exception of Exp. 20 (error, −0·0024 grm.), in which the recovery of a large quantity was carried out for the first time.

EARTH-ACID RECOVERY.—The experience gained in these investigations makes it increasingly clear that, generally speaking, the precipitation of the earth acids, followed by suitable purification of the precipitates, involves a slight negative error. Usually the loss is negligible, but it is bound to increase with the number of the fractions and with re-precipitation. Exps. 9 to 16 on the pyrosulphate tannin method furnish an example of that tendency. In the oxalate salicylate method, it is counteracted more or less by the slightly incomplete elimination of the titania, of which somewhat less than one mgrm. is found in $(P^2+\Pi^2)$ (last column of table). We feel justified, therefore, in adopting the rule that the net weight of $(P^2+\Pi^2)$, uncorrected for its small titania content, is to be taken as the nearest approach to the true M_2O_5 figure. The M_2O_5 errors in column 8 of the table, which have been computed in accordance with the above rule, prove that we are now able to carry out the separation with a reasonable degree of accuracy without recourse to the correction factors required in the earlier method (the text of pp. 323 and 324, Sect. XIV, is now obsolete). In Exps. 18 and 19, where the error exceeds the usual tolerance, the predominant constituent is tantalum-free niobic oxide, which is a rare case in mineral analysis. Where the M_2O_5 ratio is high, we recommend direct determination of the titania as well as of the earth acids, the total recovery loss being added to M_2O_5, or finally apportioned between the two pentoxides after tannin separation. To sum up, the calculated error in the oxalate salicylate method should not exceed 0·001 grm. (less than 0·5 per cent. on 0·25 grm. of mixed oxides).

Each cycle of operations requires two working days, so that the whole process can be carried out in four days. It is easy of execution, as the successful separation does not depend on delicate adjustments or fractional precipitations.

RETROSPECT.—A few remarks on the principles underlying the separation of

titania from the earth acids may conclude this final account of our investigations into the subject.

Differences in chemical behaviour which persist when the elements are in admixture, and hence may serve for their analytical separation, are of two kinds:

(1) *The earth acids do not, whilst titania does, form a soluble salicylic acid complex.* It is upon the formation of the stable crystalloidal salicylic titanium complex (*cf.* preamble to VI, ANALYST, 1926, **51**, 613) that the most efficient separation method is based.

(2) *The earth acids do not, whilst titania does, form a soluble sulphate, nitrate, and chloride.* The earlier attempts (*cf.* XII, ANALYST, 1928, **53**, 470) were based on the inability of tantalum or niobium to form a soluble sulphate, and were defeated by the strong tendency of the reacting elements to form complex hydrolysis precipitates. Tannin counteracts that tendency (XV, *loc. cit.*); hence, when the bisulphate melt is leached with acid tannin solution, titanic sulphate is dissolved, whilst the earth acids remain as insoluble tannin adsorption-complexes.

The connection between the pyrosulphate tannin method and tartaric hydrolysis may not be obvious at first sight, but, nevertheless, the two methods are based on the same difference in chemical deportment: in tartaric hydrolysis the excess of strong mineral acid breaks up the soluble tartaric complexes, with formation of insoluble earth acids and soluble titanium chloride (nitrate). Neither process possesses the accuracy of the oxalate-salicylate method, but both are valuable adjuncts, as shown in this paper and in Section XV (*loc. cit.*).

SUMMARY.—The oxalate-salicylate method for the separation of titania from the earth acids, described in an earlier paper, has now been perfected, with the result that an almost quantitative recovery of the earth acids is achieved, and that less than one mgrm. of titania remains in the final pentoxides. The process is claimed to be accurate within 0·5 per cent. The application of the pyrosulphate tannin method to the determination of small amounts of earth acid in titania is explained. The principles underlying the separation of titania from the earth acids are briefly discussed.

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

DISCUSSION

Dr. B. S. EVANS said that he would like to preface his remarks with congratulations to Dr. Schoeller on his remarkable results, not only in the present paper, but also in others of the same series. He (the speaker) had repeatedly found them indispensable when dealing with niobium and tantalum. He would like to raise one point regarding the relatively bad result put down for niobium in the separation of niobium from titanium. Would the process be safe where one got, not pure niobium, but a mixture of niobium and tantalum: that was to say, was the error, which he noticed was repeated, bound up with the absence of tantalum, and would it be put right by its presence? If so, could Dr. Schoeller give any indication of the amount of tantalum which would make it safe?

Dr. SCHOELLER, in reply, said that the recovery of the niobium appeared to be improved by the presence of tantalum, as in the last experiment shown in the Table, in which a mixture of tantalic and niobic oxides (61·4 per cent. Ta_2O_5) was used and a satisfactory result was obtained. He and Mr. Jahn had not, however, so far, been able to carry out enough work to state the minimum amount of tantalic oxide which would correct the niobium recovery.

The Determination of Chlorides in Dairy Products and Biological Material

By W. L. DAVIES, M.Sc., Ph.D., F.I.C.

(*Read at the Meeting, October 7th,* 1931.)

THE comparative ease and accuracy with which chloride can be determined suggest the application of the determinations as checks on other operations, such as control of sampling, checking of repeated samplings, and the evaluation of the volume of a precipitate. The salt content of food refuse of a variable composition, *e.g.* fish meal or hotel refuse, is of importance in the feeding of animals.

THE DRY-ASHING METHOD OF CHLORIDE ESTIMATION.—Incineration of the material, followed by a determination of the chloride in the ash, has many disadvantages, such as tendency to loss of chloride by direct volatilisation and loss of hydrochloric acid by the action of non-volatile acid oxides on chlorides. A determination by this method requires a considerable amount of time, especially when fluids have to be evaporated. The alkali chlorides are volatile at red heat,[1] and blank determinations are necessary when alkaline earth oxides are added to "fix" the chlorides.

WET METHODS OF DETERMINING CHLORIDE.—The chlorides in biological material are present as easily soluble salts, and the problem of a wet determination centres around the quantitative solution in a medium which will not interfere with the Volhard method. All colloidal material likely to react with silver salts, either by adsorption or base exchange, must be broken down, and the resulting colour of the solution must be such that the end-point in the titration can be accurately detected. The interference of other salts, such as phosphates, silicates and carbonates, can be overcome by using the Volhard method of titration exclusively. The direct titration of chloride in butter, for instance, is to be deprecated, owing to the curd absorbing silver ions.

The most convenient method of destroying organic matter is by digestion with dilute nitric acid. This has been applied by Van Slyke[2] to the determination of chlorides in blood, in place of the ashing process advised by Whitehorn.[3] The method, applied to dry material, consists in wetting the sample thoroughly with water, warming, if necessary, then adding standard silver nitrate solution in excess of the equivalent of chloride present, pure concentrated nitric acid to make the concentration about 25 per cent., and boiling the contents of the flask over gauze. In the Carius method of determining chlorine in organic compounds, even fuming nitric acid has no effect on silver chloride, since, in the presence of silver salts, the solubility of silver chloride is of a much lower order of magnitude than is likely to interfere with the accuracy of the method. The disintegration effected by nitric acid needs only to reach the stage when all

possibly interfering substances, such as proteins and complex carbohydrates, are broken down to true water-soluble compounds, to make complete wet-ashing unnecessary. Globules of free fat do not interfere with the subsequent titration and need not be removed. When removal of silver chloride, owing to its bulk, is necessary, the fat globules are also removed.

Improvement of the Colour of the Solution and the End-point.—With all material containing protein the liquid after digestion possesses a lemon-yellow to yellowish-brown colour, due to the nitration of aromatic amino-acids. Dilution of the liquid usually also dilutes the colour sufficiently to remove any difficulty in observing a sharp end-point. The elimination of nitrous acid cannot, of course, be effected by boiling the concentrated digest, and since boiling the diluted solution would unnecessarily prolong the determination, the addition of urea in slight excess is efficacious in decolorising the hot solution. This does not completely destroy the yellow colour, but it prevents the usual deepening of the colour experienced on adding iron alum solution.

The addition of urea thus removes difficulties connected with the end-point, and the addition of acetone, in amount sufficient to give a final concentration of 5 per cent., gives a still sharper end-point. In the Volhard method it is advisable to filter off the silver chloride, owing to the reaction between it and ferric thiocyanate.[4] With large amounts of silver chloride, and in the presence of much fibre, sand, and undecomposed fat, this is advantageous, in that it allows the final titration to be carried out in a liquid containing the minimum amount of suspended material, and that in strong sunlight the silver chloride darkens considerably. But with small amounts of silver chloride, and on titrating immediately and quickly after dilution, no advantage is gained by removing the precipitate. Acetone has a protective effect in preserving the colour of ferric thiocyanate, even in the presence of appreciable amounts of pyrophosphate, possibly owing to a combined solvent and oxidation effect (due to the peroxide present).

Description of the Method.—The wet method for chloride determination may be described as follows:

(*a*) *Milk* (*and Biological or other Fluids*).—Ten ml. of milk, if the result is required as mgrms. of chlorine per 100 ml., or 10 ml. weighed, if the percentage of chlorine or sodium chloride is required, are pipetted into a 250 ml. flask, and 10 ml. of 0·05 N silver nitrate solution are mixed with it. Two ml. of saturated potassium permanganate solution (approx. 6 per cent.), and 10 ml. of pure concentrated nitric acid are added, and the contents of the flask are boiled over gauze in a draught chamber until the liquid is clear (except for the small amount of precipitate) and reddish-brown fumes are copiously evolved (three to four minutes). Under similar conditions the volume of nitrous fumes varies directly with the lactose content of milk, and milk of low chlorine content (see below) and correspondingly high lactose content yields fumes more quickly and copiously than milk of low lactose or high chlorine content. A pinch of urea (0·25 grm.) is added to the hot solution, and the contents of the flask are diluted to about 100 ml. Six ml. of acetone and 1 ml. of a saturated solution of iron alum in 10 per cent.

nitric acid (prepared by boiling excess of iron alum in 10 per cent. nitric acid, cooling and filtering) are added, and the excess of silver nitrate is titrated with 0·05 *N* potassium thiocyanate (standardised upon the above-mentioned silver nitrate by means of standard potassium chloride solution). A blank determination for reagents is also made when standardising the silver nitrate. (Without exception, the above reagents have been found absolutely free from chlorides, provided *pure* nitric acid was used. Even commercial iron alum is free from chloride, but fresh samples should be tested.)

The above quantities are suitable for most samples of milk, and 10 ml. of 0·05 *N* silver nitrate solution are equivalent to 177·2 mgrms. of chlorine per 100 ml. when working with 10 ml. of milk. Some samples give a result exceeding this value, and this necessitates the addition of 15 or 20 ml. of silver nitrate before digestion. The determination takes very little time, and thirty samples can easily be dealt with in an hour. All biological and other fluids can be treated in the same way. Urine does not require boiling with acid, and the Volhard method can be used in the cold, but the silver chloride, owing to its bulk, must be filtered off.

(*b*) *Solid Material.*—A sufficient weight of material to contain 0·15 to 0·30 grm. of chlorine (combined) is weighed into a 250 ml. conical flask, and well wetted or soaked with water, warming if necessary, and 25 ml. of 0·05 *N* silver nitrate solution are added. After thorough shaking, 10 ml. of saturated permanganate solution and 25 ml. of concentrated nitric acid are added, and the contents of the flask are boiled over gauze. Starchy food disintegrates quickly, yielding a yellow solution, but foods rich in protein, especially those containing fibrous protein (*e.g.* fish meal), take longer to dissolve. If the amount of salt is considerable, or if there is a large volume of unattacked fibrous material, fat or sand, the cooled, diluted (100 ml.) digest is filtered by suction, the precipitate being washed repeatedly with hot 5 per cent. nitric acid. But when the amount of solid material is small, the excess of silver nitrate may be determined at once. The filtrate is made up to standard volume (200 ml.), and the excess of silver nitrate is determined in aliquot portions (or on the whole liquid) by titrating with 0·05 *N* thiocyanate solution, using 1 ml. of saturated iron alum as indicator, after adding acetone until the solution contains 5 per cent. In determinations in which excess of silver nitrate was not added at the outset, it is necessary to repeat the determination on a fresh amount of material; further addition of silver nitrate after acid digestion is useless.

EXAMPLES OF RESULTS.—A few examples of triplicate determinations on some common foodstuffs are given in Table I.

TABLE I.

Silver chloride not filtered off, unless stated.

(*a*) *Milk.*	A.	89·4;	89·5;	89·5	mgrms. Cl per 100 ml.
	B.	110·2;	110·2;	110·3	,, ,, ,, ,, ,,

(Samples of milk may be encountered containing from 60 to over 300 mgrms. of chlorine per 100 ml. The average range is from 70 to 130 mgrms.)

TABLE I.—*continued.*

		Sodium Chloride. Per cent.
(*b*) *Other Dairy Products.*		
Cheese.	New Zealand Cheddar	1·62; 1·65; 1·63
	English Cheddar	1·56; 1·58; 1·56
Butter.	New Zealand, salted	1·61; 1·62; 1·62
	High salt, experimental	6·13; 6·12; 6·14
Dried milk		1·99; 2·00; 2·00
Dry whey and separated milk		2·19; 2·18; 2·19
(*c*) *Other Foodstuffs.*		
Bread (white crumb)		0·956; 0·958; 0·955
Biscuit (broken)		0·110; 0·111; 0·112
*Prepared meat (paste)		3·68; 3·67; 3·68
Dried yeast		nil; nil
*Fish meal (1)		1·97; 1·96; 1·95
(2)		2·56; 2·57; 2·55

* Silver chloride filtered off.

THE VALUE OF A QUICK METHOD FOR CHLORINE DETERMINATION AS APPLIED TO OTHER OPERATIONS.—(1) SAMPLING.—The ease with which the determination can be carried out commends it as a rapid means of checking the accuracy of sampling or of checking replicated samples. It can also serve as a check on the equalisation of material in bulk and on thorough mixing, *e.g.* of milk.

Table II illustrates the application of the chloride content of milk as a test for the equalisation of the bulk milk of a large herd of cows. (This work was done during the study of a herd giving low solids-not-fat consistently; hence the low solids-not-fat figures. The examples given show the importance of equalising such milk.)

TABLE II.

Chlorine (chloride) as mgrms. per 100 ml. and percentage of solids-not-fat.

			Churn No.					
			1.	2.	3.	4.	5.	6.
1.	8/4/30 a.m.	Chlorine ..	113	122	137	122	122	—
		Solids-not-fat	8·31	8·38	7·85	8·47	8·43	—
2.	8/4/30 p.m.	Chlorine ..	117	117	127	121	—	—
		Solids-not-fat	8·38	8·50	8·39	8·42	—	—
3.	9/4/30 a.m.	Chlorine ..	114	119	116	111	129	144
		Solids-not-fat	8·49	8·45	8·52	8·56	8·01	7·77
4.	9/4/30 p.m.	Chlorine ..	118	118	119	115	—	—
		Solids-not-fat	8·30	8·30	8·44	8·45	—	—
5.	10/4/30 a.m.	Chlorine ..	123	122	123	123	123	145
		Solids-not-fat	8·34	8·51	8·48	8·46	8·41	7·73
6.	11/4/30 a.m.	Chlorine ..	118	107	112	115	120	132
		Solids-not-fat	8·34	8·48	8·52	8·44	8·54	8·01

Examples 2 and 4 show well-equalised milk. Churn 3 in Ex. 1, Churns 5 and 6 in Ex. 3, and Churn 6 in Ex. 5 and 6, show high chloride figures and low solids-not-fat content, owing to inefficient equalising.

(2) EVALUATION OF THE VOLUME OF A PRECIPITATE.—Occasionally the volume of the precipitate obtained while preparing a clear serum has to be taken into account. To obtain the copper serum of milk, 100 ml. were added to 25 ml. of copper sulphate (containing 72·5 grms. per litre), and, after shaking and leaving for five minutes, the clear serum was filtered off. On determining the chloride in the milk and serum, the volume of the precipitate was calculated:

Chloride content of milk = 113·8 mgrms. Cl per 100 ml.
,, ,, ,, copper serum = 94·4 mgrms. ,, ,, ,, ,,
or 118·0 mgrms. ,, ,, 125 ,,

$$\text{Volume of serum} = \frac{113{\cdot}8}{118{\cdot}0} \times 125 = 120{\cdot}6 \text{ ml.}$$

Hence the volume of precipitate = 125 − 120·6 = 4·4 ml.

(Woodman[5] cites 2·6 ml. as the volume of precipitate from 65 ml. of milk, or 4·0 ml. for 100 c.c. This value, of course, varies with the fat content of the sample.)

(3) CALCULATION OF THE APPROXIMATE LACTOSE CONTENT OF MILK.—The complementary relationship between lactose and chlorides in milk has evoked much discussion, and various values and constants have been suggested. Of these, "the simplified molecular constant" (S.M.C.), suggested by Matthieu and Ferré[6] (critically reviewed by Porcher[7]), is the most useful. Chlorides and lactose account for 75 per cent. of the osmotic pressure of genuine fresh normal milk, irrespective of the composition of the sample, and it is suggested that a lowering of lactose content is accompanied by an isotonic increase in chloride content, and that one grm. of common salt is equivalent in this respect to 11·9 grms. of lactose. The S.M.C. is the lactose equivalent of the common salt, plus lactose of milk in grms. per litre [or lactose (grms. per litre) plus 11·9 × NaCl (grms. per litre)], and is roughly equivalent to 70. On a percentage basis, therefore:

Per cent. of lactose + 11·9 × per cent. of sodium chloride = 7 (approximately) or
Per cent. of lactose + 19·6 × per cent. of chlorine = 7.

For a very large number of samples analysed by various workers the S.M.C. has been found to vary from 69 to 73, with a few samples outside this range. Calculation of the constant on a fat-free serum basis gives more comparable results. The constant is claimed to show a distinction between watered milks (S.M.C. falling to 65 with 5 to 10 per cent. of added water) and samples low in solids-not-fat (normal values of the S.M.C.).

From the above equations, the chloride content being known, the lactose figure can be deduced approximately. A few results are given in Table III.

TABLE III.

Sample.	1.	2.	3.	4.	5.	6.	7.
Chlorine, per cent. ..	0·075	0·086	0·100	0·168	0·169	0·178	0·188
Lactose (calc.), per cent.	5·53	5·31	5·00	3·71	3·69	3·51	3·31
Lactose (determined by copper reduction method)	5·50	5·27	5·01	3·74	3·79	3·42	3·33
S.M.C. (from lactose found)	69·3	69·6	70·5	70·3	70·9	69·1	70·2

Samples 1 to 3 were normal in composition, whilst samples 4 to 7 were low in solids-not-fat, the deficient constituent being lactose.

KOESTLER NUMBER.—Koestler,[8] studying the milk of cows when drying off, observed a rapid rise in chloride content, and, taking into account the inter-relationship between lactose and chloride content, suggested that abnormal milk was being secreted when the value $\frac{100 \times \text{Cl per cent.}}{\text{lactose per cent.}}$ exceeded 3·5 (the Koestler number). From the chloride content and the S.M.C. relationship, the value can be calculated from the expression $\frac{100 \times \text{Cl per cent.}}{7 - (19{\cdot}6 \times \text{Cl per cent.})}$. Equating this to 3·5 (as the maximum for normal milk), the chlorine content becomes 0·146 per cent., *i.e.* all samples containing over 0·146 per cent. of chlorine are abnormal. Most milk samples show a range in Koestler number of 1 to 3, corresponding with a chloride (Cl) content of from 0·070 to 0·130 per cent.

By calculating the approximate lactose content from the chlorine figure it can be deduced whether deficiency in solids-not-fat is caused by lactose or not. This can quickly be done by the rough rule that for every 0·050 per cent. of chlorine (more accurately, 0·051 grm. of chlorine per 100 ml.) the lactose content is lowered 1 per cent. from a hypothetical maximum of 7 per cent. (*e.g.* in a sample of milk containing 0·125 per cent. of chlorine, the lactose is, roughly,

$$7 - \frac{125}{50} = 4{\cdot}5 \text{ per cent.}).$$

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NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING,
SHINFIELD, READING.

DISCUSSION.

Mr. E. HINKS asked, regarding the determination of chlorine, what proof the author had that the chlorine figure he obtained was the right one. The deductions drawn from the chlorine content were extremely interesting, especially those referring to the volume of precipitate. The Milk Products Sub-Committee, when considering this, tried the chloride content as a "tell-tale" and failed, since they could not get the chloride determination sufficiently accurate, and they had to adopt other methods. He was not sure how the chloride method would work out for condensed milk. It was extraordinary that variations from 60 to 300 mgrms. of chlorine per 100 c.c. could be encountered, and surely the samples showing high values were abnormal.

Mr. BACHARACH referred to the chloride content of dried milk, given as 2 per cent. If this represented eight times the concentration of the original milk, it would mean that the chloride concentration was 0·250 per cent. in the milk, which was decidedly abnormal.

Mr. STRAFFORD asked if Dr. Davies had ever tried the electrometric method. This saved a great deal of time, and the outlay for plant was not very great.

Dr. W. L. DAVIES replied that he had tested the method by adding definite amounts of potassium chloride, and that quantitative recovery had been obtained. The volume of precipitate had also been tested half-a-dozen times with different chloride contents. The data collected for illustrating the variation of chloride content in milk arose from other researches, and the extraordinary variations of from 60 to 300 mgrms. of chlorine per 100 c.c., quoted, were obtained from the study of individual samples of milk from a herd giving low solids-not-fat figures. Such a variation would be rare in a normal herd. The chloride content of dried milk was given as per cent. of sodium chloride, which would give a normal chlorine figure if reported as chlorine per cent. With regard to electrometric methods, the conductivity method was successful, but a potentiometric method would involve clearing the solution of protein, owing to adsorptive effects.

ADDENDUM.—The end-point of the titration of excess silver nitrate in the determination of chlorides in milk is sensitive to the nearest drop, and this, with the strengths of solutions used, justifies the calculation of the chloride content only to the nearest 0·5 mgrm. per 100 ml. milk. For quick work on a large number of samples it is satisfactory, for most purposes, to determine the chloride to the nearest mgrm. per 100 ml., *i.e.*, the percentage of chloride is accurate to the third decimal place. For the same reason the limitations of the fineness of the end-point in using the method for the calculation of the volume of precipitate justify its being given only to within the limits of ±0·25 ml. in accuracy.

Oil from Malayan *Aleurites Montana* and the Properties of Hong Kong Oil

BY T. HEDLEY BARRY

(*Read at the Meeting, December 2nd,* 1931)

IN September, 1930, I received from the Director of Agriculture, Federated Malay Straits and Straits Settlements, a 5-lb. sample of kernels collected from *Aleurites montana* trees growing at the Experimental Station, Serdang, which were planted during March, 1925. The seeds from which these trees were grown were obtained from the Botanical and Forestry Department, Hong Kong. The fruits were collected on August 8th, 1930, and the kernels were air-dried for ten days before despatch.

From the economic point of view the experiments in Malaya have not been satisfactory so far, and the authorities have come to the conclusion that *Aleurites montana* is not suited for cultivation in the plains of Malaya.

A description of the growth and condition of the trees up to the end of 1928 was published by J. N. Milsum and T. D. Marsh (*Malayan Agric. J.*, 1929, No. 2, p. 47).

Although the ultimate result of the experiments was not entirely satisfactory, the trees made rapid growth during the early stages, and the results of an examination of the oil extracted from the kernels collected in 1928 from three-year-old trees were published by C. D. V. Georgi and G. L. Teik (*Malayan Agric. J.*, 1928, No. 8, p. 296).

Apart from the purely scientific interest attaching to these experiments, the examination of oil from *Aleurites montana* is of practical importance. It is known that the oil from S. China, which is generally sold under the name "Hong Kong" oil, is derived from two species of *Aleurites*—*A. Fordii*, Hemsl, and *A. montana* (Lour), Wilson.

According to E. H. Wilson (*Bull. Imp. Inst.*, 1913, **11**, 441), the bulk of the oil exported is obtained from *A. Fordii*. Recently an important paper has been published by F. A. McClure (*Lingnan Sci. J.*, 1930, **9**, 233), giving an account of his tour of the Provinces of Kwangtung, Kiangsi, Anhwei, Kiangsu and Hupeh, which covered some of the most important areas in which the tung oil tree is cultivated.

According to McClure the cultivation of *A. montana* is confined largely to the provinces of Kwangtung and Kiangsi. Oil from this species is, therefore, to be expected in the commercial article exported from Canton or Hong Kong.

It has long been recognised in the trade that Hong Kong wood oil is of different quality from that generally known as Hankow oil. The difference is doubtless mainly due to the greater care in extraction and purification exercised at Hankow, where the Americans, in particular, have established trading centres.

At the same time the fact that Hong Kong oil is admittedly derived from two species of trees suggests the possibility that the oil from *A. montana* is not absolutely identical with that from *A. Fordii*. The oil examined by Georgi had the following characteristics:—Sp. gr., 0·939; acid value, 3·6; saponification value, 195·5; iodine value (Wijs), 160·3; unsaponifiable matter, 0·6 per cent.; refractive index at 20° C., 1·5098. The most notable feature in these results is the low refractive index. The figure, however, was confirmed by the Department of Agriculture, F.M.S. and S.S., the refractive index being kindly re-determined at my request on the 29th October, 1930, and found to be 1·5097 at 20° C., which is practically the same as the published figure. The most obvious explanation of this abnormally low refractive index would appear to be that the trees were not developing normally, with the result that the oil was of a somewhat different composition from that of the normal product.

Oils obtained from *A. Fordii*, grown in China and in Kenya, have been examined, and the results are summarised in the *Bull. Imp. Inst.*, 1930, **28**, 268, and in no case is a refractive index lower than 1·518 at 20° C. recorded. The lowest recorded refractive index for an authentic *A. Fordii* oil, so far as I am aware, is 1·5155 for a Californian cold-pressed oil (David Fairchild, Circ. 108, *Bull. Plant. Ind.*, Washington, 1913), but this was considered an unusual sample, the seed having been stored for over a year. The few samples of oils from *A. montana* which have been reported show a considerable variation in this respect.

Aleurites montana.	Refractive index at 20° C.
Burma[1]	1·4755
Japan[2]	1·5221
China, 1929[3]	1·5134
1930	1·5164
Malaya[4]	1·5098

[1] *Indian Forest Records*, 1923, **10**, Pt. 2, p. 11.
[2] *Trav. Lab. Mat. Med.*, Paris, 1926, **17**, 24.
[3] *Bull. Imp. Inst.*, 1930, **28**, No. 3, p. 270.
[4] *Malayan Agric. J.*, 1928, **16**, 296.

Aleurites Fordii.	Refractive index at 20° C.
China (*a*)	1·5229
(*b*)	1·5204
Kenya	1·5194

(*Bull. Imp. Inst.*, 1930, **28**, No. 3, p. 268.)

The oil from the present sample was, therefore, examined, with particular reference to these points, and also to the possibility of this apparent difference between the two oils having some bearing upon the difference between the commercial oils from Hong Kong and Hankow.

EXPERIMENTAL.—The oil was extracted from the beans both by pressure and by cold extraction with petroleum spirit (b. pt. 40° to 60° C.).

Extraction by pressure was effected in a small hand-press, giving about 1½ tons per square inch. By the first method 42 per cent. and by the second **19·2** per cent. of oil were obtained. The total oil-content was determined by extraction with boiling petroleum spirit (Georgi and Teik found 43·2 per cent.). The meal from the hand-press was extracted with cold petroleum spirit.

The oil extracted with petroleum spirit both from the pressed meal and from the original beans proved very retentive of the solvent, and isomerised much more rapidly than did the cold-pressed oil. Even when kept in the dark, it set almost solid in the course of a few weeks, whilst that obtained by pressure remained perfectly clear and liquid when kept in a plain bottle, although, of course, not exposed to the direct action of light.

In order to remove the last traces of solvent from the extracted oil, it was necessary to pass steam through it for some minutes. After this treatment the oil was dried and filtered.

REFRACTIVE INDEX.—The following results were obtained on the various samples:

		Refractive index at 20° C.
(1)	Solvent-extracted, (*a*) before steaming	1·5086
	(*b*) after steaming	1·5128
(2)	Cold-pressed	1·5135
(3)	Solvent-extracted from pressed cake and steamed to remove solvent	1·5125

For comparative purposes, the following results were obtained with samples of Chinese oils, from *A. Fordii* and *A. montana*, and from American *A. Fordii* :—

		Refractive index at 20° C.
(1)	Chinese *Aleurites montana*	1·5160
(2)	Chinese *A. Fordii*	1·5190
(3)	American tung oil, Corporation Standard	1·5190

The sample of Chinese *montana* oil was crushed by a firm in Hull from seeds obtained from China, and I am indebted to Dr. L. A. Jordan, Director of the Research Association of British Paint, Colour and Varnish Manufacturers, for the sample.

As regards the Browne Test, it is evident that all the samples of *montana* oil reported polymerise much more slowly than oils from *A. Fordii* (*Bull. Imp. Inst.*, 1930, **28**, 268).

Aleurites montana.		Browne test. Minutes.
China	(*a*)	24·0
	(*b*)	20·5
Burma		16·0

For the oils extracted from the Malayan kernels the results were:

	Minutes.
Cold-pressed oil	$15\frac{3}{4}$
Solvent-extracted	$18\frac{1}{2}$

Parallel tests with Chinese and American oils gave:

	Minutes.
Chinese *A. montana*—hot-pressed	$11\frac{3}{4}$
Chinese *A. Fordii*	$9\frac{3}{4}$
American *A. Fordii*	$9\frac{1}{4}$

IODINE VALUE.—The iodine value was determined by the method of Wijs (1 hour at 22° C.), and the thiocyanogen value by Kaufmann's method (*Ber.*, 1929, **62**, 392; ANALYST, 1929, **54**, 304), the following results being obtained:

Malayan *A. montana*—	Wijs' method.	Kaufmann's method.
(*a*) Cold-pressed	163	81·1
(*b*) Solvent-extracted from pressed meal	160	78·6
(*c*) Solvent extracted from beans	—	81·4
Chinese *A. montana*	—	81·3
American *A. Fordii*	166	82·7

From the above results it appears that the oil from *A. montana* has a consistently lower refractive index than oil from *A. Fordii*, and that trees growing in unsuitable districts may yield an oil of even lower refractive index than the normal Chinese *A. montana*. It should, however, be borne in mind that the number of samples of authenticated botanical origin which have been examined is still too small to justify dogmatic assertion on this point.

As regards refractive index, the lower limit generally accepted, in both Europe and America, is 1·518 at 20° C., and, therefore, none of the samples of *montana* oil from the kernels referred to in this paper would pass the specification.

Regarding polymerisation, apart from the Chinese *montana* oil, which just falls within the specified limit (12 minutes), all the *montana* oils take considerably longer than *Fordii* oils. In this connection it is of importance to note that the consistence of the jelly is equally, if not more, important than the time of setting. In the case of these *montana* oils, it was noted that the jelly, though distinctly softer than that from Hankow oils or from *A. Fordii*, was not sticky, and its general condition was much firmer than that which is obtained from Hankow or *Fordii* oils adulterated to give a setting time of the same order as *montana* oil.

As to the bearing of these results on the properties of Hong Kong oil, as distinct from Hankow oil, one would expect that the presence of *A. montana* oil

would reduce the refractive index and increase the polymerisation time. The oil from *A. montana* may be more liable to variation than that from *A. Fordii*, and much more information is necessary before the limits of variation in its analytical constants can be fixed.

In this connection, however, a recent report by A. R. Penfold and F. R. Morrison (*Bull.* 12, Technological Museum, Sydney) on a series of Australian-grown *A. Fordii* is of interest as indicating that the oil from *A. Fordii* also varies considerably in properties according to the condition of the tree. The refractive indices of the samples examined by these workers vary widely, and the oils obtained by solvent-extraction in several cases show a lower refractive index than corresponding samples obtained by pressure, *e.g.* the oil (25 per cent.) extracted by pressure had the refractive index (25° C.) 1·5152, whilst the oil (52 per cent.) solvent-extracted had the refractive index 1·5133. Some of the solvent-extracted oils also appear to have isomerised very rapidly.

Hong Kong Oil.—It is well known that varnish makers differ in their opinion as to the value of "Hong Kong Oil," some refusing to use it, whereas others apparently find no difficulty in making satisfactory products with it. Varnish-making, however, is so complicated and varied a process, and the personal factor plays so large a part in determining the results, that it is impossible to say how far the objections to Hong Kong oil are due to prejudice and local usage or to physical characteristics, such as colour and freedom from "foots," which could be remedied by improved methods of extraction and refining, or whether there is a fundamental difference in composition which has an effect on the resulting varnish.

Satisfactory varnish can undoubtedly be made from Hong Kong oil. Considerable quantities of the oil are used both in this country and on the continent, although, normally, Hong Kong oil fetches a somewhat lower price than Hankow oil.

As to the analytical constants of Hong Kong as distinct from Hankow oil, little has been published. China wood oil, shipped through Hong Kong, is examined by the Government Laboratory, and I am much indebted to Mr. E. R. Dovey, the Government Analyst, for his cordial assistance in giving information as to the work in Hong Kong. The specification of the "Association of Exporters and Dealers of Hong Kong" for South China wood oil is as follows:

"Specific gravity .. .. not less than 0·9400 at 15° C.
Refractive index .. .. ,, ,, ,, 1·5184 at 20° C.
Total impurities (dirt, moisture, etc.) .. less than 1 per cent.

In addition, the oil shall pass an accepted polymerisation test—either Worstall, Browne, Bacon or Chapman."

The Browne Test, the originator of which was formerly Government Analyst at Hong Kong, is used in the Hong Kong Laboratory. In the case of 80 per cent. of the oil passing through Hong Kong, samples are taken by Government analysts, but as regards the rest, a sample is frequently sent to the laboratory, in which case, of course, no guarantee as to the authenticity of the sample can be given.

It is rather remarkable to note that, although Hong Kong oil is considered inferior, and the authenticated oils from *A. montana*, so far examined, show the peculiarities of comparatively low refractive index and slow polymerisation, the specification drawn up by the Hong Kong Laboratory, which deals particularly with oil from the districts in which *A. montana* grows, actually sets a higher standard in the matter of refractive index than do either European or American laboratories for "Hankow oil," which is considered to be the purer grade and consists essentially of oil from *A. Fordii*.

McClure was able to establish the fact that the Chinese in the regions he visited were well acquainted with the distinction between the two trees. The name "T'ung Yau Shue" is applied to both *A. montana* and *A. Fordii*, but where both species grow together distinctive names are used.

In Kiangtung, *A. montana* is known as "Ten Thousand Year Tung"—"Maan Nin T'ung," and *A. Fordii* as the "Three Year Tung"—"Saam Nin T'ung" or the "Early Rice Tung"—"Tso Woh T'ung," the *A. Fordii* maturing more rapidly in South China than the *A. montana*, though, apparently, it is not so long lived.

In Anhwei, however, the name "Maan Nin T'ung" is said to indicate trees which bear fruit in three years, but in this province only *A. Fordii* appears to be cultivated. Deliberate adulteration of the oil by the native pressers was formerly common, but all the Chinese buyers are now equipped with refractometers, and, consequently, adulteration in that quarter, at least, has practically ceased, though, as the natives use the same press for all oil seeds, the presence of small amounts of other oils is inevitable, and of these, cottonseed oil is said by a Hankow authority to be the most common.

A recent report on the Economic Condition of China (*Dept. Overseas Trade*, Aug. 1930), however, rather tends to destroy confidence in this statement. Apparently, modern factories are now established at Chingking, Changtuh and Wanhsien, where the oil is refined and shipped in bulk by way of Hankow.

Some 8000 tons were shipped in this way in 1929, and the amount is increasing. It is stated, however, that there has been a notable fall in the quality of the Chinese oil, and that the practice of adulteration, which was formerly common at the collecting centres, is now practised to an increasing extent by the natives themselves in the inland districts.

I have had occasion to examine a number of Hong Kong oils which had been shipped to this country during 1930, and, with the exception of one batch of about ten tons (concerning which an unsuccessful claim for adulteration was made), had been absorbed by the paint and varnish trade in Europe without complaint.

The result of the examination of 23 samples may be summarised as follows:

	Maximum.	Minimum.	Average.
Acid value	11·27	3·23	7·04
Refractive index at 20° C. ..	1·5172	1·5153	1·5162

The specific gravities (at 15·5° C.) of seven of these samples were determined, with the following results:—Maximum, 0·9436; minimum, 0·9411; average, 0·9420.

A detailed examination of eleven of these samples gave the following results:

	Browne test. Minutes.	Acid value.	Refractive index. (20° C.)
1.	11	3·23	1·5158
2.	11	3·46	1·5159
3.	$12\frac{3}{4}$	7·21	1·5160
4.	$12\frac{1}{4}$	6·70	1·5160
5.	12	8·23	1·5156
6.	$10\frac{1}{2}$	3·08	1·5172
7.	$12\frac{1}{2}$	8·56	1·5153
8.	$11\frac{3}{4}$	6·46	1·5168
9.	$10\frac{1}{2}$	3·22	1·5178
10.	$12\frac{1}{4}$	7·73	1·5160
11.	$11\frac{1}{2}$	7·57	1·5155

As was to be expected, the samples with the higher acid value showed a longer time of polymerisation. Standard samples of China wood oil, examined under the same conditions, gave a result of about 7 to 8 minutes. The refractive indices were in every case below the limit of 1·518, so that none of them, as judged by the ordinary standards, would be regarded as above suspicion, merely on the strength of these figures.

Correspondence with the Government Laboratory at Hong Kong revealed the fact that samples alleged to have been taken from the bulk deliveries of these oils had been submitted to the Government Laboratory and passed as being in accordance with the specification, but in no case had the sample been taken by the officials of the Laboratory.

Mr. Dovey was also good enough to re-determine the refractive indices of all the samples relevant to the shipments in question. In all, thirty samples were examined.

	Max.	Min.	Average.
Original Hong Kong oil, refractive index	1·5209	1·5182	1·5192
Re-determined, August 14th, 1930 ..	1·5210	1·5182	1·5191

The difference between the original and the re-determined refractive indices varied from −0·0007 to +0·0003. Only two samples showed the extreme variation of −0·0007, and, generally, the variation was of the order of ±0·0002. The results are of some interest as showing that the refractive indices of the oil do not alter to any appreciable extent on storage under normal conditions, even in the Tropics. It would also appear from these results that the native dealers use their refractometers to good effect and that, whatever may be the nature of a shipment, the sample which goes to the Government Laboratory is certain to pass the specification, and too much importance need not be attached to the Government report, unless the sample is actually taken by a properly accredited official.

As a general conclusion from the samples which I have examined, it would appear that Hong Kong wood oil frequently has a refractive index below the accepted minimum of 1·518, and that this may be due to the presence of oil from *A. montana*. It is not, of course, possible to come to a definite conclusion from a comparatively few samples which come from one source, but it would seem of some importance to investigate the matter further, with a view to definitely establishing

this point. It is not suggested that the standard of the present specification should be reduced, but, if further investigation shows that the oil from *A. montana*, as obtained by the Chinese on a commercial scale, has normally analytical constants of the order of the values discussed in this paper, its presence in Hong Kong oils would account for the results here recorded, and the question how far the low refractive index and longer polymerising time are to be taken as indicating a lower quality, as distinct from adulteration, is, therefore, of some interest. Whilst the production of tung oil remains in the hands of the Chinese, it would seem impossible to separate the oils of the two species on a commercial scale, and, therefore, the oil of *A. montana* must be accepted as a normal constituent of the tung oil from the regions in which both species grow.

There is at present no recognised method of directly determining the presence of *montana* oil in China wood oil, and more work upon the characteristic properties of these two oils is a matter of considerable importance and interest. Whether the difference between the oils of the two species is sufficient to be of practical importance to the varnish maker—assuming, of course, equality as regards purity, etc., in other respects—is open to discussion.

THE LABORATORY,
84, FETTER LANE, E.C.4.

DISCUSSION

Mr. E. R. BOLTON said that the difficulty arose from the fact that most natural products exhibited natural variations, and, whilst the variations in a substance like milk were well known to every member of the Society, variations in tung oil were not so clearly appreciated. He hoped that the time was not far distant when tung oil would be bought and sold upon the proportion of elaeostearic acid, as being the constituent upon which its commercial value depended. The Imperial Institute had formed a Committee on tung oil (of which he was chairman); this, with financial aid from the Empire Marketing Board, had done much to encourage the production of tung oil in the Empire. He, therefore, sincerely trusted that no idea would arise that tung oil from British colonies was an inferior article, as it certainly was not. Mr. Bolton took the view that the discovery that certain oils obtained from *A. montana* were of lower quality than the average did not justify the author's suggestion that the standards should be widened and lowered. The Hong Kong Government Laboratory had recently taken steps which would most certainly have the effect of making adulteration more difficult, and it would be deplorable if we were to make it easier.

Mr. C. E. SAGE said that when adulteration of wood oil became prevalent, some 20 years ago, a method of sampling had been worked out, which, he thought, had considerably reduced the percentage of adulterated oil in commerce. In the case of commercial oils some definite relationship between analytical values and quality had been established, but for "home made" samples of oil one had to consider another set of standards altogether, for commercial oil must of necessity undergo some changes on keeping. Such oils might contain 5 to 6 per cent. of free fatty acid, but, personally, he avoided oils which contained over 3 per cent. Regarding the work done by the author of the paper, they were dealing with material obtained from young trees, and that would naturally differ from oils obtained from old-established trees which had been in the ground for years.

Dr. H. E. COX enquired whether there was any physiological explanation of the fact that oils obtained from immature trees, or, speaking generally, from trees grown in warmer countries, should have lower iodine values and refractive

indices than those grown in colder climates. Apparently, the further south one went, the lower became these figures.

Mr. K. A. WILLIAMS thought that the variation of the constants of this Malayan oil from those of the Chinese oil was partly a climatic effect, as the characteristics of all oils were governed to a large extent by the temperature at which the plant grew. For example, linseed oil, having an iodine value of 180, could be produced in England, but soya bean oil, with an iodine value of 130, could not, because it required a slightly warmer country. If any particular oilseed were grown in different places, it was found that the colder climates produced oil of higher iodine value than the warmer ones; the exact constitution of the oil depended on the needs of the plant for the conditions under which it grew.

Mr. BARRY, replying, said that it would be seen from the figures quoted in the paper that excellent results had been obtained with oils from some parts of the British Empire, but, on the other hand, the unsatisfactory results obtained with oils from other parts were equally important from the scientific point of view.

The experiments showing the effects of local conditions upon China wood oil were particularly valuable, in view of the fact that the composition of that oil differed so remarkably from that of the seed oils with which it was often associated in industry.

In this connection the remarks of Dr. Cox and Mr. Williams were very suggestive. In the case of the ordinary seed oil the life cycle of the plant was completed within a single season, and the oil produced contained a series of aliphatic glycerides of varying degrees of unsaturation. It would appear that the plant, to some extent at least, adjusted itself to conditions by a variation in the proportion of the individual glycerides present in the oil. In the case of China wood oil, however, the life history of the tree producing it covered many years, and the oil consisted almost entirely of a single glyceride, namely, that of elaeostearic acid, which was characterised by its extreme sensitiveness to changes in physical condition and by an arrangement of its double-bonds which was unique among vegetable oils.

One would expect, therefore, that climatic and other conditions would have extremely interesting effects on the nature of the oil produced. As Mr. Sage had suggested, the age of the tree might also be expected to influence the nature of the oil to some extent, but it had to be admitted that the results obtained in America, where the subject has been most fully investigated, did not indicate that the difference was very material, providing, of course, the tree was properly cultivated and not exploited before reaching a reasonably mature age. It was not impossible that with increased knowledge of the properties and the best method of cultivation, commercially useful results might be obtained even in Malaya, although, for the time being, experiments had been discontinued.

The author was fully in agreement with Mr. Bolton that a distinction must be drawn between adulterated and abnormal oils. From the point of view of the consumer, the botanical origin of the oil was immaterial, for he was merely concerned with the properties which influenced the quality of his finished product, and the question, therefore, was not so much a matter of condemning oils as of grading them. If the acceptance or rejection of oil bought by a contract were based solely upon whether or not deliberate adulteration had been practised, the existence of dubious samples was a continual source of trouble and expensive litigation. On the other hand, if supplies were purchased on a definite specification, this question of adulteration was, to a large extent, avoided. At the same time, the analyst could not ignore the existence of abnormal samples, whether dealing with China wood oil or with other natural products. The recognition of the distinction between abnormal and adulterated samples not only determined the attitude of the State towards the producer of the article in question, but also made it possible to trace the cause of abnormality to its source, and in most cases eventually to reduce, if not entirely to eliminate it.

Experiments on the Quantitative Separation of Pilocarpine from Quinine by Means of Gallotannin

By M. NIERENSTEIN, D.Sc.

(*Work done under the Analytical Investigation Scheme*)

In a previous communication from this laboratory (Fear, Analyst, 1929, **54**, 317) it was shown that, of twenty-six alkaloids examined, only quinine, cinchonine, cinchonidine, strychnine, brucine and caffeine were precipitated by gallotannin. This suggested the possibility that gallotannin might prove a quantitative reagent for the separation of these two types of alkaloids, and pilocarpine and quinine were chosen as representative examples. Unfortunately, it was found at an early stage of the investigation that as much as 15 to 18 per cent. of pilocarpine could not be accounted for when precipitating, with gallotannin, the quinine from a solution containing pilocarpine (base) and quinine hydrochloride. This discrepancy, as subsequent work has proved, is due to the fact that quinine gallotannate (and this will probably also apply to the other gallotannates) adsorbs pilocarpine.

1. Preparation of Quinine Gallotannate.—The gallotannin used was purified according to Fischer (*Ber.*, 1912, **54**, 915) and tested for *free* gallic acid by Mitchell's method (Analyst, 1923, **48**, 2), as modified by Nicholson and Rhind (*ibid.*, 1924, **49**, 507). It contained 3·8 per cent. of gallic acid, but it was found that by prolonged washing with ether the free gallic acid content could be reduced to 0·7 per cent., after which further washing with ether seemed to have no further effect. The quinine gallotannate was prepared by adding a 2 per cent. solution of gallotannin solution to a 1 per cent. solution of quinine hydrochloride in water, collecting the precipitate with the aid of a suction pump, washing with ether, and drying at 100° C. Quinine gallotannate is hygroscopic, and is best kept in a vacuum desiccator over phosphorus pentoxide.

2. Determination of Pilocarpine.—Solutions of 2 grms. of pilocarpine (base) in 100 c.c. of distilled water were used in all the experiments. Such a solution has $[\alpha]^{18}_{D} = +106°$ according to Schmidt (*Die Alkaloide,* 1920, p. 580), but, as the result of a series of observations made in this laboratory, the constant $[\alpha]^{18}_{D} = +109·5°$ was adopted. The aqueous solution (50 c.c.) was extracted four times with 50 c.c. of ether free from alcohol (B.D.H. Purified Ether, sp. gr. 0·720), and the collected extracts were dried over sodium hydroxide for ten days and evaporated. The residue was then left standing in a vacuum desiccator for eight days over paraffin, until constant in weight. The error, based on 28 determinations, was found to be $\pm 1·3$ per cent.

3. Action of Quinine Gallotannate on Pilocarpine.—Solutions of pilocarpine (50 to 125 c.c.) were shaken for 2 to 16 hours with quinine gallotannate

(2 to 12 grms.), filtered and extracted with ether, proportional quantities of ether being used. In this manner it was found (32 determinations being made) that 8·3 to 19·2 per cent. of pilocarpine had been adsorbed by the gallotannate, the adsorption apparently depending on the length of time of shaking.

It might be pointed out that the quinine gallotannate does not undergo disintegration during the process of adsorption, since the rotation of the pilocarpine, if interpolated, remains $[\alpha]_{D}^{18} = + 109{\cdot}5°$ when adsorbed by quinine gallotannate. This was found to be the case in all the experiments mentioned above. Since quinine is laevorotatory, there would have been a fall in the rotation if quinine had been set free. The values obtained for pilocarpine, after adsorption by quinine gallotannate, are thus not affected by the presence of quinine.

BIOCHEMICAL LABORATORY,
UNIVERSITY OF BRISTOL.

Notes

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

DETECTION *IN SITU* OF TIN SOLDER CAUSING DARK DISCOLORATION IN CHEESE

SAMPLES of cheese showing areas of dark pigmentation around specks of foreign material are occasionally encountered. The cause may be due to small particles of lead-containing material slowly dissolving and diffusing through the cheese, lead sulphide being deposited by the interaction of small amounts of hydrogen sulphide formed during cheese ripening (Leitch, *Scot. J. Agr.*, 1927, **10**, 165). Cheese may be contaminated with traces of lead or lead compounds either as a rare impurity in annatto (in coloured cheese), as red lead from pipe joints, or as abraded solder from unions, seams or other source. The detection of lead in the amount necessary to cause the trouble in cheese is difficult, often indefinite, and sometimes impossible (see the "triple nitrite test" described by Fairhall, *J. Biol. Chem.*, 1923, **57**, 455). But when such cases are due to particles of solder, advantage can be taken of the sensitive "molybdenum blue" test for the tin accompanying the lead in the solder (Munro, *Proc. Nov. Scot. Inst. Sci.*, 1927, **16**, 9). The test can be carried out *in situ* on the dark areas in a thin section of cheese.

A section of cheese showing darkened area and, if possible, the exposed nucleus, is moistened with water on a watch glass, and a drop of 0·5 per cent. solution of ammonium molybdate in *N* hydrochloric acid is added, followed by a drop of 5 per cent. sodium phosphate solution (bench reagent). If tin is present, an intense blue colour will develop in a short time around the nucleus, growing fainter towards the edges of the patches. The blue colour will be seen to concentrate in the veins between the particles of curd, which stand out clearly against the darker blue boundaries. A positive test for tin in the dark patch is an indication that solder is present, the lead of which is responsible for the discoloration. Cheese not contaminated with tin in this manner does not develop any blue colour, only a faint green tinge forming within an hour of carrying out the test.

The metals likely to get into cheese during manufacture are tin, lead, iron and copper. If a particle of copper (metal) is embedded in cheese, its presence in the

ripened cheese will be shown by the formation of a strong *green* halo round the particle. This would be true for any copper alloy, also. This has been met with in practice.

Particles of iron or of iron rust do not form black discolorations; and, although the particles are often discernible to the naked eye, they are looked on as "dirt," or "foreign matter," and classed with particles of straw, rubber, etc., as accidental impurities.

Lead is the metal causing discoloured areas which usually are responsible for lowering the marketable value of the cheese, and the object of the present note is to detect the entry of solder into cheese by testing for tin. The tin in cheese is undoubtedly in the stannous condition, since (*a*) the oxygen tension in cheese is of a very low order, and oxidation of stannous salt would be improbable, and (*b*) tin slowly dissolving from metallic tin would be in the stannous condition. Even exposure of a section of cheese to the air for a considerable length of time before testing would not change the tin salt into the stannic condition, especially in the presence of elementary tin in the nucleus.

W. L. Davies.

National Institute for Research in Dairying, Reading.

Legal Notes

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

SUITABILITY OF WATER SOFTENER FOR HAIR-DRESSING PURPOSES

On October 20th, 1931, a claim was brought by a firm of engineers in the High Court before Sir W. Hansell, K.C., Official Referee, for the balance of the price of an automatic water-softening machine which had been supplied to a firm of hairdressers. The defendants admitted the claim, but pleaded that the machine produced water which was wholly unsuitable for their purposes, as it could not be used for waving hair, but left it sticky.

Dr. H. S. Hatfield pointed out what he regarded as defects in the plaintiffs' machine.

An assistant in the hairdresser's firm gave evidence that after water from this machine had been used the hair was sticky and could not be combed, and there were complaints of the "permanent wave" coming out in a week. When natural soft water was used there were no complaints, and complaints stopped after the use of this machine was discontinued.

Mr. C. E. Sage, F.I.C., said that he had analysed the water in question. He would not describe it as soft water, but as "treated" water, which he would not care to drink. His objection to it was the absence of lime and the presence of soda.

Mr. W. H. Simmons, B.Sc., F.I.C., said that he had experimented with human hair immersed in water containing 17 parts per 100,000 of sodium carbonate, and was of opinion that such a water as was produced by this softener would not adversely affect the process used by the defendants. Such water was also, he considered, perfectly suitable for human consumption.

On October 26th, Sir W. Hansell, giving judgment, said that the description given by the selling agent of the plaintiffs, who said that the machine was automatic and suitable for hairdressers, did not amount to a warranty, but was only of the nature of description, persuasion and puff. The machine was automatic, and any trouble in its working appeared to be due to the fact that when it was installed the defendants had not appreciated the fact that the water pressure was not suitable. The defendants had failed to satisfy him that anyone had suffered any ill effects through drinking the water, and, in any case, there was no warranty that the water was potable.

There was considerable conflict of evidence as to whether the water was fit for the purpose of hairdressing, and the defendants had failed to satisfy him that it was not suitable. If he had to decide why there were occasional failures in the hair-waving operations, he would say that they were due either to the health of the lady on whom the wave refused to stay, or to the fact that the soap had not been sufficiently rinsed away. If he were wrong, the sum of £20 would amply compensate defendants for any damage sustained. There would, therefore, be judgment for the plaintiffs.

A stay of execution was granted with a view to an appeal.

New South Wales

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930

THE Acting Government Analyst (Mr. S. G. Walton) reports that 22,194 samples were examined during the year ending December 31, 1930, of which 19,705 were samples taken in connection with the Pure Food Act, 1908. By far the greater proportion of the food samples were milks, of which 14,638 (351 adulterated) were collected in the Metropolitan area, and 2747 (159 adulterated) in country districts. Among the subjects dealt with in the Report are the following:

BUTTER SUBSTITUTES AND THE MARGARINE STANDARD.—Samples of "butter" submitted were found to contain large proportions of coconut fat. This was apparently part of a systematic attempt to evade the provisions of the regulations governing butter and margarine (butter substitutes). The standard for margarine requires that all preparations of edible oil or fat which are intended to be, or which may be, used in place of butter, shall be marked "Margarine," and, also, to permit of easy identification, the standard requires that such preparations shall contain specified proportions of sesame oil or Queensland arrowroot. The butter-fat content, moreover, is limited to 10 per cent. When an article is prepared for use as butter, which is not marked "Margarine," and which does not contain the ingredients specified in the standard for margarine, it must be in conformity with the requirements of Regulation 27, *i.e.* it must be butter. The samples under notice were not marked "Margarine," did not contain either Queensland arrowroot or sesame oil, and approximately 25 per cent. of butter was present as one of the constituents. The following is a representative analysis:—Water, 15·8; curd and salt, 2·3; fat, 81·9 per cent. The values from the fat were: Reichert–Wollny value, 13·9; Polenske value, 13·0; Kirschner value, 6·5; iodine value, 9·5; and saponification value, 251. From these results it was concluded that the fat was prepared chiefly with coconut fat, and contained approximately 25 per cent. of butter.

STANDARD FOR CITRUS FRUIT JUICES.—The extraction of citrus fruit juices for the cordial trade is almost wholly done by mechanical means. There is, therefore, a tendency to include with the juice, rind, pith and segment partition walls

in a finely divided state. For the purpose of prescribing the maximum amount of insoluble solids which should be allowed in citrus fruit products (beverages), analyses were undertaken, the results of which are given hereunder. The method used was that given in the "A.O.A.C. Methods of Analysis" (1925 edition, p. 210), for water-insoluble solids in fruit products, excepting that, before weighing, the insoluble matter was separated from the hardened filter paper used, by washing it with a jet of hot water into a dish in which it was evaporated to dryness and weighed. The following results were obtained:

	Insoluble solids. Per Cent.
Orange juice (a good mechanically extracted juice)	1·0
Lemon juice („ „ „ „)	0·6
Lemon juice expressed in laboratory (1 doz. lemons of average quality were deprived of their skins, and, as far as possible, freed from adhering pith. They were then pulped, this pulp containing all the coarse segment partition walls and juice cells)	2·2
Lemon juice expressed in laboratory (1 doz. lemons of similar quality to those above were squeezed in an ordinary glass squeezer. This juice represents an ordinary lemon squash containing practically all the juice cells, but not the segment partition walls)	0·5

After consideration of these figures it was decided that, in order to prevent the addition of rind, pith and segment partition walls to citrus fruit juices, the following standards should be recommended:

Orange juice: Insoluble solids to be not more than 1·5 per cent.
Lemon juice: „ „ „ „ „ „ „ 1·0 „

STANDARD FOR JAM.—With a view to formulating a suitable standard for jam, samples differing in quality were examined, the following results being obtained:

	Strawberry conserve. Per Cent.	Strawberry conserve. Per Cent.	Raspberry jam. Per Cent.	Raspberry jam. Per Cent.
Moisture (loss at 100° C.)	21·5	42·9	20·65	25·56
Total solids	78·5	57·1	79·35	74·44
Insoluble solids	1·0	1·6	3·13	3·18
Alcohol precipitate (pectin, etc.) ..	0·27	0·39	0·24	0·31
Total acidity (as citric acid)	0·59	0·60	0·90	0·82
Malic acid .. Not more than	0·1	0·1	0·1	0·1
Citrates (as citric acid)	0·72	1·07	1·09	1·27

The question of permitting the addition of various fruit derivatives to jam, with a view to improving manufacture without lowering the quality, was considered. Where the fruit used, through seasonal or other cause, is deficient in those natural qualities (acid, pectin, etc.), on which the flavour and appearance of the finished product depend, it appears reasonable to allow the addition of limited amounts of these substances in order to ensure the manufacture of a better and more uniform article. Moreover, recent investigation has shown that acid is necessary for the conversion of pectose into pectin. As, however, the indiscriminate use of acid and pectin might result in lessening the quantity of fruit used, it is necessary, if the use of these substances is to be sanctioned, to prescribe a minimum fruit content. After consideration of all the facts, it was recommended that the standard should provide for a fruit content of not less than 45 per cent. (by weight), and should permit the addition of up to 0·3 per cent. of pectin (calculated as calcium pectate) and of 0·5 per cent. of fruit acids.

USE OF SAPONIN IN BEVERAGES.—During the year a sample of "heading," used for promoting froth on beverages, was received for analysis. This was found

to be a solution of saponin, probably obtained from quillaia bark. The saponins derived from this source are stated to contain toxic glucosides (quillaic acid and sapotoxin), and the presence of any glucoside must, in accordance with the requirements of Regulation 66 (1), be declared on the label.

Substances similar to this have been universally used for the production of froth on temperance and other drinks for a very long period. Although saponin has well-defined toxic properties, it is recognised that the mucous membrane of the digestive canal forms an almost complete protection to limited amounts of it, and, therefore, it is unlikely that harmful results would ensue from the quantities at present being used in beverages. If, however, its continued use is to be allowed, it is desirable that the maximum amount permissible should be specified.

Experiments as to the toxicity of the sample submitted were carried out as follows:—A guinea pig weighing 472·5 grms. was "drenched" with 1 c.c. of the sample, and was not affected after twenty-four hours. The same animal was then "drenched" with 5 c.c. It showed extreme distress after one and three-quarter hours, and died within two hours. On examination the stomach showed a large patch of haemorrhage in the wall; congestion in the upper third of the intestines; slight congestion of the spleen and liver. The kidneys and suprarenals were normal. The stomach and part of the intestines were very considerably distended with froth, and the heart was very full. Apparently the immediate cause of death was the pressure on the heart from the enormously distended stomach.

Saccharin in Food.—The substitution of saccharin for sugar has lately become increasingly noticeable. An examination of pickles, made in 1929, disclosed the fact that practically all the locally-made articles contained this substance, manufacturers urging in its favour that the public demanded white, sweet pickles, which could only be supplied by the substitution of saccharin for sugar in manufacture. It was stated that when sugar is used, reaction with acetic acid causes discoloration and renders the article unattractive.

In 1930 it was found that saccharin was used by manufacturers in this State in the preparation of ice-cream cones. The reason given for the substitution in this instance was that cones containing the requisite amount of sugar became soft on exposure, and in that condition proved unsatisfactory containers for ice cream.

A representative number of cordials was examined for the presence of saccharin, but in only two cases, both of which were of country manufacture, was saccharin found.

Persulphates in Bread Improvers.—Four samples of yeast foods submitted were found to contain persulphate in amounts ranging up to 3 per cent. The use of this "improver" in flour is a recent innovation in this State, and was the cause of a severe outbreak of bakers' dermatitis in employees handling these substances. Action has been taken, as a consequence of which the use of persulphates as a constituent of yeast foods has been abandoned.

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1930

The Government Analyst for Cyprus (Dr. S. G. Willimott) reports that the year 1930 was the busiest since the Government Laboratory was opened in 1901, because of the re-organisation of the laboratory and the construction of separate laboratories for analytical work, forensic investigations and water analysis. The

official work consisted of the usual analyses and examinations in connection with criminal cases, counterfeit coins, samples under the Food and Drugs Law of 1926, samples for water analysis, customs and excise, animal viscera for poison and a miscellaneous collection of samples for private analysis. The total number of analyses made was 1546, as compared with 1713 in 1929, the reduction being due to pathological specimens now being dealt with in the Bacteriological department, so that the year's analytical work shows an increase of 50 per cent. Some 631 exhibits were examined in connection with 168 criminal cases.

HASHISH TRAFFICKING.—It is some years since so many important cases of trafficking in hashish, contrary to the Dangerous Drugs Law, were investigated. Three such cases came before the District Court of Limassol. In each case the material in question was identified as hashish of second quality, probably originating in Syria. The defence that this material was some substance other than hashish failed in each case and convictions were recorded.

FORENSIC WORK FOR THE POLICE.—Under the present system many frivolous, even ridiculous, cases are sent in indiscriminately by the Police for investigation, and it is calculated that only about 6 per cent. of this work is of any real value to the Crown. In Palestine, where a very similar problem arose, the difficulty was solved by placing with the Attorney-General's Department the authority for having exhibits examined in the Laboratory.

MUSHROOM POISONING.—An investigation of poisonous fungi arose in connection with two important outbreaks of mushroom poisoning at Lefkoniko and Larnaca; in the former case ten people died, and in the latter one person. From the forensic point of view, the Larnaca case was of special interest because an alkaloid of the nature of muscarine, the poisonous principle of certain fungi, was isolated from the viscera. By investigating the species and habitat of both edible and inedible species of Cyprus mushrooms, it was possible to carry the investigation a stage further. Poisonous types were also examined for their content of alkaloids of the muscarine group.

COUNTERFEIT COINS.—The 54 counterfeit coins examined appear to fall into two distinct categories, *viz.* one consisting of coins composed of practically pure tin, and the other of coins of silver and copper, the silver varying between 60 and 80 per cent. This comparatively high percentage is probably explained by the low price of silver at present prevailing.

BARIUM CARBONATE IN ANIMAL POISONING.—Eighteen viscera, taken from ox, sheep, mule or donkey, were analysed, but one only (sheep) was found to contain a poisonous substance. This was identified as barium carbonate. This chemical finds considerable use in Cyprus as a rat poison, and accidental poisoning of animals by this means is very liable to occur.

FOOD SURVEY OF CYPRUS.—A food survey of Cyprus was carried out during the last six months of the year. The objects of the survey were to ascertain, as accurately as possible, the real adulteration rate prevailing in the Colony and to obtain sufficient analytical data on local products to frame scientific standards for the staple foodstuffs. Accordingly, a large number of samples was collected both in town and village throughout the six administrative districts. It was arranged, through the police, to take samples every week in the Nicosia district, and every fortnight in the five remaining districts. Altogether, 610 official samples were analysed during this experiment, that is, the largest figure recorded for any half-year. The minimum rate of adulteration found was 8·3 per cent., which figure will probably be increased when the milk data, which it is hoped to obtain in 1931, can be included in these results. As in previous years, the principal commodity adulterated was coffee, 49 of 163 samples being condemned.

WATER SUPPLY OF CYPRUS.—There can be no question that this is one of the most urgent sanitary problems in Cyprus to-day. Of 70 samples arising from all six districts, six were found on analysis to be unfit for drinking purposes. The samples examined this year included many from new sources of supply located principally in the villages. Increasing knowledge of local water supplies indicates the impossibility of applying any rigid European standards to Cyprus waters. Indeed, to do so would be equivalent to condemning most of the water sources in the Island. It is true that both chemical and bacteriological data point to the existence of very pure water supplies in the mountain areas, but only too frequently such waters become more or less contaminated by the time they reach the consumer, the root of the trouble being the incidental contamination of unprotected water-courses, faulty aqueducts or open wells. There is undoubtedly great need in Cyprus for a scientific water survey, especially as no official standard of any description exists for potable water-supplies.

"CRUDE PETROLEUM."—Thirty-nine samples were submitted by the Customs and Excise Department as "crude petroleum," according to the Law. Some difficulty arose in connection with the samples coming within this category. The importation of solar oil as fuel for gas engines increased very considerably during the year, and since it was found, as the result of laboratory tests, that it frequently gave a reasonable illumination when burnt in an ordinary lamp, the oil in question became legally dutiable. This imposed some hardship on the farmer, who was the principal consumer, and created an obstacle to agricultural development. The real difficulty, however, lies in the unsatisfactory condition of the law as it relates to petroleum products. A confusion of terms appears to have sprung up, namely, to confuse crude petroleum, as it exudes from the well, with the various less refined petroleum products, ranging from solar oil to Diesel oil. The difficulty may be removed either by evaluating such petroleum products on the basis of analysis and by the recognition of definite scientific standards, or by remitting altogether the duty on petroleum products other than kerosene and benzine.

Commonwealth of Australia

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

DIVISION OF FOREST PRODUCTS*

No. 1. IDENTIFICATION OF WOOD BY CHEMICAL MEANS. PART I

The limitations of methods of identification of woods are emphasised, with special reference to the hardwood genus *Eucalyptus*, of which over 300 species are known in Australia. Chemical tests, which may supplement microscopical methods, are reviewed. Thus, Kanehira (*Bureau of Productive Industries, Formosa*), estimates flavone content from the colour produced on reduction of 10 c.c. of an alcoholic extract of the wood in the presence of hydrochloric acid, magnesium powder and a drop of mercury, and so places the wood in one of 3 categories according to the intensity of the colour. Welch (*J. and Proc. Royal Soc., N.S.W.*, 1922, **56**, 241) has also attempted to distinguish groups of this genus by tests on aqueous and alcoholic extracts with reagents such as ferric chloride, sodium hydroxide, lime water, etc., but the method requires further systematisation and standardisation on a large number of samples of known origin, especially in cases where the species are botanically similar (*vide infra*).

* Technical Papers, Nos. 1, 2 and 3, 1931. Nos. 1 and 2, by H. E. Dadswell; No. 3, by W. E. Cohen and H. E. Dadswell.

Improved tests on the lines of Welch's experiments showed that considerable variations may occur even with different samples from the same species, but that previous knowledge of the chemical composition may assist in the development of a simple test.

IDENTIFICATION OF KARRI (*E. diversicolor*) AND JARRAH (*E. marginata*).—(1) The standard procedure of the U.S. Forest Products Laboratory was employed (Schorger, *Chemistry of Cellulose and Wood*, 1926), and 34 samples of jarrah and 17 of karri were shown to have cellulose contents (on an oven-dry basis) of 35·4 to 51·6 (mean 44·5) and 53·0 to 62·7 (mean 59·0) per cent., respectively. (2) A simpler test is to burn a splinter of the untreated sound heart-wood the size of half a match. Karri (150 samples) burned well, with glowing, to a white ash, whilst jarrah (200 samples) always burned poorly without glow, and left little or no black ash. (3) The ash content of 5 grms. of sawdust was determined by ignition in a platinum dish, the residue was dissolved in excess of warm 0·1 *N* hydrochloric acid, and the mixture was back-titrated with 0·1 *N* sodium hydroxide solution to phenolphthalein. Karri (29 samples) gave 0·12 to 0·86 (mean 0·30) per cent. of ash, having an alkalinity of 0·33 to 1·57 (mean 0·63) c.c. of 0·1 *N* acid per grm. of oven-dry wood, and jarrah (58 samples) 0·04 to 0·49 (mean 0·14), and 0·00 to 0·16 (mean 0·06), respectively. These methods, especially (2) and (3), are effective only if unweathered and untreated wood is used; weathering changes the ash content to a greater extent than the cellulose figure.

IDENTIFICATION OF TALLOWWOOD (*E. microcorys*), BLACKBUTT (*E. pilularis*) AND WHITE MAHOGANY (*E. acmenioides, carnea* and *umbra*).—(1) The mean ash contents were 0·27, 0·16 and 0·09 per cent., and their alkalinities 0·42, 0·05 and 0·02 c.c., respectively. In one (abnormal) case only was the alkalinity of a tallowwood ash lower than those of the other two species. (2) About 2 grms. of sawdust are heated with 20 c.c. of alcohol for 2 minutes, and the extract is cooled, filtered and diluted with 20 c.c. of water. Tallowwood gave a definite white turbidity, blackbutt a clear solution, and white mahogany an immediate turbidity which, unlike that from tallowwood, was subsequently filterable.

IRONBARK GROUP (15 samples).—Ash-alkalinity values were:—*E. sideroxylon, propinqua* and *punctata*, below 0·16 c.c.; *E. paniculata*, above 0·78 c.c. (49·0 to 56·0 per cent. of cellulose); *E. siderophloia*, 0·35 to 0·05 c.c.; *E. crebra*, 0·90 to 0·32 c.c. (35·4 to 46·3 per cent. of cellulose). The dilution test is positive for *E. sideroxylon* only.

RED BOX (*E. polyanthemos*) AND RED GUM (*E. rostrata*).—If 0·5 c.c. of a 1 per cent. solution of sodium hydroxide is added to 5 c.c. of an alcoholic extract of the sawdust after pre-extraction in hot water, yellow and chocolate-coloured precipitates are produced, respectively (7 samples).

NO. 2. DENSITY OF AUSTRALIAN TIMBERS

The sp. gr. of the solid woody material constituting timber is 1·52, though that of the actual timber depends on the number, size, form and arrangement of the wood cells. These cells contain water and shrink on drying, and methods for the determination of density must take such shrinkage and water into account. Methods are usually based on the weight of the oven-dried sample in relation to the volume after oven-drying, or on similar ratios for air-dried or green (*i.e.* the living) wood, the last being of value only when green timber is available (see "Methods of Testing Small Clear Specimens of Timber," *Brit. Eng. Stds. Assoc.*, Specification No. 373, 1929). Modification of these methods are also used.

None, however, is suitable for the identification of Australian timbers, since these differ in moisture-content, and, in some cases, it is unlikely that two pieces of wood from the same stick will collapse on drying in the same way. The oven-dry weight and volume after soaking were therefore determined instead.

Method.—Three adjacent cross-sections (0·25 to 0·5 inch thick), cut at least 2 inches from one end of the block, were kept together and trimmed to $2{\cdot}5 \times 1$ inch, so as to obtain only sound heartwood. All were then immediately scraped free from dust and splinters and placed in an air-tight container, the two outer blocks (M) being weighed together and heated at 105° C. until constant in weight, whilst the centre portion (D) was immersed in water until it had attained a constant volume (*e.g.* 6 days if 11 per cent. of water was originally present). D was then wiped dry on the outside, and the new volume was determined in the usual way from the displacement, as given by the buoyant force exerted by the sample when immersed in water. Then oven-dry weight of D=(original weight of $D \times$ oven-dry weight of M)/(original weight of M); and sp. gr. $= 62{\cdot}5 \times$ (calc. oven-dry weight of D)/(volume after soaking) in lbs. per cubic foot. It was shown that even with highly dried *E. regnans*, a timber in which collapse on drying is very prevalent, soaking causes the volume to return to its "green" dimensions. Green samples should be given the same treatment, since slight collapse may occur even with high moisture-contents. Determination of oven-dry weight after soaking is not recommended, owing to the possible loss of extractives, nor is it advisable to use the same piece of timber for both oven-drying and soaking, unless the sample is very small, in which case the former value should be determined first.

Data.—*E. crebra*, 56·1 (mean sp. gr. in lbs. per cb. ft.); *sideroxylon* (red ironbark), 54·9; *siderophloia*, 57·4; *paniculata*, 55·7; *polyanthemos*, 54·9; *rostrata*, 43·6; *resinifera*, 45·9; *gomphocephala*, 51·4; *patens*, 42·7; *redunca* (var. *elata*), 57·9; *accedens*, 57·4; *salubris*, 55·1; *salmonophloia*, 56·0; *tereticornis*, 48·5; *marginata* (jarrah), 41·6; *sieberiana*, 45·8; *obliqua*, 35·4; *gigantea*, 34·1; *regnans* (mountain ash), 27·9; *pilularis*, 44·3; *microcorys*, 51·8; *diversicolor*, 37·9 to 46·1. The values for karri and jarrah are lower than those obtained by the oven-dry weight/volume method. The sp. gr. decreases slightly with increase in height of the sample from the ground (about 3 units between 5 and 35 feet).

No. 3. Study of Lignin Determination

According to the U.S. Forest Products Laboratory (Mahood and Cable, *J. Ind. Eng. Chem.*, 1922, **14**, 251), 2 grms. of air-dried sawdust (80 to 100-mesh) are extracted for 4 hours with a mixture of benzene and alcohol (2 : 1) to remove resins, gums, kinos, etc., and the residue is dried and digested for 16 hours with cold 72 per cent. sulphuric acid. The acid is then diluted to 3 per cent., the mixture boiled under a reflux condenser for 2 hours, and the final residue (lignin) filtered on a tared alundum crucible, washed free from acid with hot water, dried at 105° C. and weighed. The method appears to be successful with North American hardwoods, but Australian woods gave high lignin contents with wide variations for one species. This was shown by microscopical methods to be due to dark-coloured substances in the vessels, ray cells, wood parenchyma and lumina of the wood-fibres, which are only partly soluble in the mixture of benzene and alcohol, and in the acid, and are therefore weighed with the lignin. Qualitative tests with various organic and inorganic solvents led to the following procedure:—

Sampling.—The standard (U.S.) method is unsatisfactory, since the above resinous materials are brittle and grind to a fine powder which tends to pass to a disproportionate extent through the finer sieve. An entire block was therefore sawn into strips and ground in an impact mill until the whole sample (about 200 grms.) passed a 100-mesh sieve. The mill failed to grind a small amount which was rejected.

Method.—About 3 grms. of sample in a 300-c.c. conical flask with an air-condenser were heated with 100 c.c. (150 c.c. for jarrah) of 0·125 N sodium hydroxide solution for 80 minutes on the water-bath, and the residue was filtered off at once in a tared alundum crucible and washed free from alkali with hot water. The

washing could be expedited by one preliminary wash with 10 per cent. acetic acid. In the experimental work the residue was dried at 105° C. and weighed in order to determine the alkali-soluble material, but, normally, the lignin determination by the standard acid digestion method is carried out on the washed residue.

Weaker alkali is not recommended, since it requires a longer digestion period, whilst stronger solutions may attack the wood structure. Successful results were obtained with Canadian hemlock (26·4 per cent. on the oven-dry weight of the original sample), Canadian spruce (24·8), jarrah (21·7), red ironbark (20·5), and mountain ash (21·4). Lignin in hemlock and spruce is more resistant to the alkali than that in the other woods, although with these the attack is so slight that the accuracy of the method is hardly affected. The above results were confirmed by microscopical methods.

J. G.

United States Department of Agriculture

SERVICE AND REGULATORY ANNOUNCEMENTS

STANDARD FOR CANNED TOMATOES*

CANNED tomatoes are the normally flavoured and normally coloured canned food consisting of the peeled, cored, and trimmed, whole or large pieces of the mature red fruit of the tomato vine (*Lycopersicum esculentum*), with or without the drained juice of peeled, cored, and trimmed tomatoes in amount not exceeding that normal to the fruit being packed, and with or without added seasoning (sugar, salt).

Meaning of Terms.—The fruit shall be considered as whole or in large pieces when at least 45 per cent. of the total contents will be retained after draining for two minutes on a sieve[1] having 2 meshes to the inch. On containers of less than 3 pounds net weight, sieves 8 inches in diameter are used. On containers of 3 pounds net weight or more, sieves 12 inches in diameter are used.

The fruit shall be considered normally coloured when a sample at least 1 inch deep of the homogeneous pulped meats shows a red colour containing at least 58·0 per cent. red and not more than 37·3 per cent. green, in terms of the three primary colour distribution curves of the Optical Society of America, referred to Abbott-Priest standard white light.[2] In performing this test the material retained on the 2-mesh sieve is pulped and freed from air bubbles. It is then placed in a black container, and visible seeds are removed by skimming or pressing below the surface.

The fruit shall be considered as peeled when there are not more than 1·5 square inches of peel per pound of net contents.

The fruit shall be considered as trimmed when the total exposed area of unsightly blemishes, such as scars or brown or black coloured portions, does not exceed one-fourth square inch per pound of net contents.

Substandard Designation.—Canned tomatoes which fail to meet the above standard shall, except as hereinafter provided, bear the legend for low quality promulgated by the Secretary of Agriculture.

Exceptions.—Canned tomatoes which fail to meet the above standard only in that they contain added pulped and strained tomato material need not bear the low-quality legend if labelled "tomatoes with purée from trimmings."

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* Food and Drug No. 1, Rev. 4, issued May, 1931, p. 6.

[1] Wire of a uniform diameter, not less than 0·04 nor more than 0·07 inch.

[2] These percentages do not refer to the proportion of "red" to "green" tomatoes in the container. They are rather the precise physical terms necessary to define colour accurately in a legal standard. Conformity to the minimum colour requirement may be conveniently judged by certain commercial colour measuring devices. For example, the colour of a given sample may be matched by the following combination of Munsell colour discs:

(1) 5R 2.6/13 (glossy finish). (3) N 1/ (glossy finish).
(2) 2.5YR 5/12 (glossy finish). (4) N 4/ (glossy finish).

If the exposed area of disc (1) covers one-third or more of the circle, and the exposed area of disc (2) does not exceed that of (1), the sample meets the minimum colour requirement, regardless of the exposed area of discs (3) and (4).

STANDARD FOR SALT.*

1. Table salt (dairy salt) is fine-grained crystalline salt containing, on a water-free basis, not more than 1·4 per cent. of calcium sulphate ($CaSO_4$), not more than 0·5 per cent. of calcium and magnesium chlorides ($CaCl_2$ and $MgCl_2$), nor more than 0·1 per cent. of matters insoluble in water.

Pending further announcement, no exception will be taken by the Food and Drug Administration to table salt that meets the requirements of the standard except that it contains anhydrous calcium sulphate (anhydrite) in excess of 0·1 per cent., provided that the total calcium sulphate content does not exceed 1·4 per cent.

STANDARD FOR BAKING POWDER.*

Baking powder is the leavening agent produced by the mixing of an acid-reacting material and sodium bicarbonate, with or without starch or flour.

It yields not less than 12 per cent. of available carbon dioxide.

The acid-reacting materials in baking powder are: (1) Tartaric acid or its acid salts, (2) acid salts of phosphoric acid, (3) compounds of aluminium, or (4) any combination in substantial proportions of the foregoing.

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* Food and Drug No. 2 (Second Revision), issued September, 1931, p. 19.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Eggs Rich in Iodine. A. Jaschik and J. Kieselbach. (*Z. Unters. Lebensm.*, 1931, **62**, 572–575.)—The whites and yolks of 14 eggs are mixed well with lime water in a large iron dish and dried at 100° C., and the residue is ground with lime water, sodium carbonate and excess of a mixture of magnesium oxide and acetate, and again dried and gently ignited. The mixture is then extracted with hot water, and any residue is again gently ignited and extracted, the combined aqueous extracts being finally evaporated and ignited once more at a low temperature. This new residue is extracted with hot alcohol and then dissolved in 2 c.c. of water, and this solution is acidified with phosphoric acid, and a drop of fresh 0·1 per cent. solution of sodium nitrite is added. If the mixture is then shaken in a stoppered tube (8 cm. long and 12 mm. in diameter, with a capillary 3 cm. long and 8 mm. in diameter at one end) with about 0·5 c.c. of carbon tetrachloride for every 0·25 to 1·00 mgrm. of iodine present, the solution of iodine in the solvent may be transferred to the capillary portion by centrifuging, and the colour matched against that produced by a similar procedure from a standard solution (Zahoránszky, after von Fellenberg, *Volksernährung*, 1930, **5**, 323; *cf.* Andrew, ANALYST, 1930, **55**, 269). Larger quantities may be titrated. The ordinary eggs of Leghorn hens (mean weight of shell 8·3, white 31·6, and yolk 18·9 grms.) yielded 24·2γ of iodine per kilo. or 1·4γ per egg, of which only a trace came from the white. Addition of the equivalent of 1·5 mgrm. of iodine per day to the diet of each hen for 2 months produced an egg with a thinner shell (mean weight 7·1 grms.), containing 31·1 grms. of white and 18·3 grms. of yolk.

The iodine content was 2·981 mgrms. per kilo., or 168·5γ per egg (15·6γ in the white, and 152·8γ in the yolk). Other authors (*loc. cit.*) have found 10 to 63γ per kilo. (0·5 to 2·5γ per egg) for ordinary eggs. J. G.

Determination of the Colouring Matter of Egg-Yolk. A. Terényi. (*Z. Unters. Lebensm.*, 1931, **62**, 566–571.)—Lutein, $C_{40}H_{56}O_2$, the yellow colouring matter of egg-yolk and an isomer of xanthophyll, is best determined by thorough extraction of 1 to 2 grms. of the ground yolk (separated from the white and shell) with three 30-c.c. portions of a mixture of equal volumes of alcohol, ether and petroleum spirit. Any lumps are broken up with a glass rod, and, after 15 to 30 minutes, each successive mixture is filtered into a 50-c.c. flask until this is filled to the mark. The colour of this extract is matched in a Walpole type of colorimeter against that of a solution in boiled water of 100 to 1000γ of potassium dichromate per c.c.; 1000γ $K_2Cr_2O_7$ per c.c. = 10γ lutein per c.c. Lutein is readily soluble in ether, acetone or chloroform, moderately soluble in carbon disulphide or methyl or ethyl alcohol, and sparingly soluble in petroleum spirit. It decomposes to the extent of 50, 11 and 18 to 20 per cent., respectively, in air at 35° to 40° C., in a vacuum at 19° C., and after standing for 24 hours in the dark in solution in the above-mentioned mixture of solvents, and it is, therefore, important that the period of extraction should be less than 30 minutes. If any foreign colour is present, the usual form of compensation-cell, containing a solution having the same colour, should be added to the colorimeter. The yolks from 6 eggs contained 0·0093 to 0·0186 per cent. of lutein (*i.e.* 1·5 to 2·6 mgrms. per yolk), the error of the method being about ±0·4γ per c.c. for 4 to 13γ of lutein per c.c. Solutions of carotene in the above solvent mixture (1 to 5·5γ per c.c.) are stable for a day, and, when fresh, are equivalent in colour to a solution of lutein about 25 per cent. higher in concentration. J. G.

Characterisation of Aldehydic and Ketonic Sugars by Oxidation with Bromine. F. Zanelli. (*Giorn. Chim. Ind. Appl.*, 1931, **13**, 514–515.)—Precise conditions are given for rendering quantitative the qualitative test proposed by Bertrand (*Compt. rend.*, 1909, **149**, 225) for characterising aldoses and ketoses. A solution of 0·1 to 0·15 grm. of the sugar (previously hydrolysed, if a polysaccharide) in 10 c.c. of water is treated with 25 c.c. of glacial acetic acid containing 10 per cent. of bromine, and kept for 24 hours in a closed vessel in the dark. The bromine is then expelled on a water-bath, and the solution is accurately neutralised with sodium hydroxide. Any residual sugar in the solution is determined by means of Fehling's solution. Under the above conditions, ketonic sugars withstand the oxidising action of the bromine, whereas the aldehyde group of aldehydic sugars is completely oxidised. Results thus obtained with sucrose, raffinose, laevulose, dextrose, galactose, and xylose, are given. T. H. P.

Method of Distinguishing Jams made from Fresh and Dried Plums and their Mixtures. P. Rudolph and H. Barsch. (*Z. Unters. Lebensm.*, **1931**, **62**, 581–582.)—Kapeller, Praege and Rademeister (*id.*, 1930, **59**, 191) recommend the addition to a filtered 10 per cent. solution of the jam of a tenth of its volume of lead acetate solution, when jams made from fresh plums give a pale or apple-green

precipitate, and those from dried plums a brown precipitate. The method is not suitable for mixtures of the two types of jam, and the present authors recommend a method based on the greater enzymic reduction capacity of fresh jams. Ten c.c. of a 10 per cent. filtered solution are maintained for 1 minute at 50° to 60° C. with 1 c.c. of 0·02 *N* iodine solution, and 20 drops of a 1 per cent. solution of starch are then added to the cool mixture. Fresh jams show no reaction (since the iodine is reduced), and dried products give a blue colour. Alternatively, the jam extract may be mixed with 10 drops of a reagent made by dissolving 0·5 grm. of magenta (diamant fuchsin) in 250 c.c. of warm water, adding 12·5 grms. of crystalline sodium sulphite and 7·5 c.c. of 25 per cent. hydrochloric acid, and diluting to 500 c.c. On the addition of 3 drops of 30 per cent. sodium hydroxide solution, jams made from dried plums remain unchanged, whilst jams from fresh plums are coloured red-brown. These reactions are capable of detecting 20 and 10 per cent., respectively, of dried plum jam in fresh plum jams. A brown colour is also obtained with fresh plum jam, but not with dried plum jam, on addition of 30 per cent. sodium hydroxide solution or of 25 per cent. ammonia in the absence of the magenta and sulphurous acid. J. G.

Crystallisation of Honey and the Heating of Crystallised Honey. H. W. de Boer. (*Chem. Weekblad,* **1931**, **28**, 682–686.)—According to Gubin (*Archiv für Bienenkunde,* **1926**, **7**) all extracted honeys contain small "primary" crystals from which crystallisation of the honey normally originates. Counts of the numbers of these showed that, for a heating period of 1 day, the number is independent of the temperature (−12° to +45° C.) at which the honey is stored, but that after 6 to 10 days the number increases with temperature to a maximum at about 10° C., and then decreases; the number for 40° C. is then approximately equal to that for −12° C. The average sizes of the nuclei in microns were 40 (star-shaped), 80 (stars and needles) and 5 (needles only) after 14 days at 0°, 20° and 37° C., respectively. On these and other grounds it is concluded that crystallisation does not originate from Gubin's primary crystals only, but that, on storage, other (secondary) nuclei form at a rate which is a maximum at 5° to 7° C., the maximum rate of actual crystallisation of non-heated honey being at about 15° C. (*vide supra*). Both the rates of formation of nuclei and of crystallisation, therefore, depend on the temperature, the maxima in the two cases being about 10° C. apart. The rate of crystallisation (V) may be calculated from the ratio of dextrose to non-sugars, and the values summarised in the table below are in agreement with the behaviour of the samples. The changes in chemical composition which occur on heating were also investigated, and the ratio 100 × fructose to dextrose was shown to increase by 6·2, 0·24 and 1·8 for fruit-tree blossom, rape-seed and for clover and cornflower honeys, respectively, after 6 hours at 70° C. Crystallised honey was also heated in tubes under varying conditions of time and temperature, and curves relating the length of crystalline portion after various heating-periods fall into 2 groups:—(*a*) The length falls rapidly in the first 10 hours and remains unchanged for a further 14 hours (temperature 60° to 80° C.). (*b*) The length rises to a maximum after about 16 to 20 hours, and then falls (45° to 55° C.). Crystallised honey may be rendered fluid by heating (*cf.* Fiehe, *Z.*

Unters. Lebensm., 1926, **52**, 244), but will re-solidify in less than 3 months unless maintained at 60° C. for 4 to 5 hours, or at 65° C. for 2 to 3 hours; below 60° C. even 24 hours' heating will not suffice. The final conclusion is that the decrease in viscosity and sucrose content and the transformation of β- into α-glucose on heating tend to increase V, whilst the corresponding decreases in dextrose content and rate of nuclei formation decrease it.

Honey.	Sucrose. Per Cent.	Dextrose. Per Cent.	Fructose. Per Cent.	Ratio of 100 F:D.	Non-sugars. Per Cent.	*V*.
Rape seed	3·5	36·78	38·78	105·4	1·64	22·4
White clover	1·2	35·97	40·66	113·0	3·38	10·6
Heather	1·7	30·83	41·17	133·5	5·18	5·9
Non-crystallising honey (1)	3·8	33·25	39·8	119·7	6·68	4·9
Non-crystallising honey (2)	2·6	26·19	44·94	171·6	6·77	3·9

J. G.

Simplified Test for the Diastase Content of Honey, and Detection of Foreign Honey by Pollen Analysis. J. Prescher and E. Bohm. (*Z. Unters. Lebensm.*, 1931, **62**, 583–585.)—The authors' experiments (*id.*, 1931, **61**, 504) have shown that in their method (*loc. cit.*) the starch value corresponding with the production of a red colour is, on an average, one-sixth of that corresponding with a blue colour (*i.e.* the diastase value). The test may, therefore, be simplified by adding to 3 separate 5-c.c. portions of 20 per cent. honey solution 1, 2 and 3 c.c. of a 1 per cent. solution of starch. After 1 hour at 40° to 42° C. the solutions are cooled, 3 drops of a 0·02 *N* solution of iodine in potassium iodide solution are added in each case, and the colours are noted. Then 6, multiplied by the limiting number of c.c. of starch solution which give a reddish colour, is the diastase value. If this is 12 or less, Gothe's test (ANALYST, 1916, **41**, 312) should be applied. Identification of the pollen structures in honey from a botanical point of view may often supplement chemical analysis in the determination of the place of origin of a honey (*cf.* Griebel, *Z. Unters. Lebensm.*, 1931, **61**, 275). Examples are given. J. G.

Freezing-Point Depression of Honey. J. Stitz and B. Szigvárt. (*Z. Unters. Lebensm.*, 1931, **62**, 506–509.)—The errors involved in the experimental determination of the freezing-point depression of a solution may be considerably diminished by cooling the solution regularly. The temperature of the cooling mixture used should be not more than 3° C. below the freezing point to be measured, and the stirring of the solution under examination should be regular and not too vigorous. Very energetic stirring results in the introduction of large amounts of air into the solution, and in consequent raising of the freezing-point by 1° to 2° C. Exceptional difficulties are met with in examining solutions of high concentrations, such as honey, which is a supersaturated sugar solution of high viscosity, and has an ill-defined freezing-point. Preliminary dilution of the honey is, therefore, necessary. Measurements of the freezing-points of aqueous solutions of honey of different concentrations show that the normal molecular depression for the solvent (water), *viz.* 1·85° C., is obtained with a 19·71 per cent. solution. The depression is caused almost entirely by the sugars; the ash, protein, acid and other components having very low concentrations. Although dextrose and laevulose are

isomeric, they produce different freezing-point depressions at the same concentration, the values for 15 per cent. (by weight) solutions being, respectively, 1·86° and 2·29° C. (sucrose, 1·10° C.). The freezing-point depression for a honey solution of definite concentration must, therefore, depend on the ratio between the percentages of dextrose and laevulose, as well as on that of water in the honey. The depression found for a 15 per cent. solution of a honey is in very close agreement with the sum of the depressions of the three sugars, as given in Landolt and Börnstein's Tables. T. H. P.

Acid Constituents of Wines. II. L. Semichon and M. Flanzy. (*Ann. Falsificat.*, 1931, **24**, 516–534; *cf. Ann. Falsificat.*, 1930, **23**, 5).—The volatile acidity of a wine is taken as the acidity due to fatty acids of the series $C_nH_{2n}O_2$, and may be divided into free and total volatile acidity, excluding acidity due to carbon or sulphur dioxide. In order to be certain that none but volatile fatty acids are being dealt with, it may be necessary to determine any lactic acid, before and after distillation, since proportions of the order of 0·76 to 1·22 per cent. of the lactic acid may be carried over; for this determination the chromic acid oxidation method is recommended, and the acid (expressed as sulphuric acid) is subtracted from the total volatile acidity. To determine the volatile acidity, 50 c.c. of wine are saturated with chalk, concentrated to half the volume, and, after cooling, acidified with a large excess of a concentrated solution of tartaric acid to liberate the free and combined volatile fatty acids. The liquid is filtered after one hour, the residue is washed with four portions of 5 c.c. of boiled water, the filtrates are made up to 50 c.c., and 10 c.c. (corresponding to 10 c.c. of wine) are used for the Blarez distillation method (Blarez, *Vins et Spiritueux*, 1908, p. 131). The carbon dioxide is driven off by boiling on the water-bath. The acidity of the distillate is determined by the author's standard method or by titration with calcium hydroxide solution, using litmus as indicator. If the esterified volatile fatty acids are to be included, the original 50 c.c. of wine, saturated with calcium carbonate, should be heated beneath a reflux condenser for one hour before reducing the volume to one-half. Corrections for sulphurous acid (by titration of sulphur dioxide liberated by sulphuric acid with 0·02 *N* iodine solution) and for salicylic acid (by addition of 1 per cent. ferric ammonium sulphate solution and comparison with standards) are made as necessary. *Formic Acid.*—For this determination, the solution of acids, obtained as above by the Blarez distillation method, is saturated with a slight excess of calcium carbonate and concentrated to 20 c.c., and 5 c.c. of this liquid are added to a cooled mixture of a chromic acid solution (100 grms. per litre) and 5 c.c. of sulphuric acid (1·71 sp. gr.). After 15 to 20 minutes the formic acid is completely oxidised, and the excess of chromic acid is titrated with a solution of ferrous ammonium sulphate. Any lactic acid present will be included as formic acid. *Butyric and Higher Acids.*—These are determined in another 5 c.c. of the wine, which is slowly evaporated to dryness, and 2 c.c. of boiled water and 5 c.c. of the chromic oxidising mixture are then added, drop by drop, the mixture being kept cool. The flask, which is furnished with a long vertical tube to act as condenser, is kept at 55°–60° C. for an hour; under these conditions the butyric and higher acids, together with any lactic acid present, are completely transformed into acetic

acid, which is then determined by ferrous ammonium sulphate. *Propionic Acid.*—Five c.c. of the same mixture are dried as described above, the chromic acid reagent is added directly to the residue, drop by drop, with cooling, and the mixture is heated on a boiling water-bath for an hour, when the propionic acid is transformed into acetic acid, as well as the lactic and higher acids, whilst the formic acid is oxidised to carbon dioxide and water. The chromic acid remaining is then determined. *Acetic Acid* is obtained from the difference between the total of the above acids (expressed as acetic), and the total volatile acidity. D. G. H.

Determination of Residual Sugar in Red Wines. J. Dubaquié and G. Debordes. (*Ann. Falsificat.*, 1931, **24**, 477–484.)—Determination by actual fermentation of the residual sugar in a wine as a means of ascertaining the possibility of the wine undergoing after-fermentation is slow, and sometimes gives uncertain results. The cupric reduction method is recommended, use being made of the two solutions: (1) 4 per cent. copper sulphate solution, and (2) a solution containing 20 grms. of Rochelle salt and 15 grms. of carbonate-free sodium hydroxide per 100 c.c. A mixture of 20 c.c. of each of these solutions is boiled for 3 minutes with 10 c.c. of the wine (containing not more than 10 grms. of reducing sugars per litre), the precipitate formed is washed by decantation, and the washings are filtered through an asbestos filter. The cuprous oxide is dissolved in 5 c.c. of dilute (1 : 2) hydrochloric acid, and the solution is treated with 2 c.c. of 10-volume hydrogen peroxide solution, sufficient sodium hydroxide solution to neutralise the 5 c.c. of acid, and 10 c.c. of solution (2). The blue liquid thus obtained represents a Fehling's solution, the sugar equivalent of which is then determined by means of a solution containing 5 grms. of invert sugar per litre. The following table gives, for each 0·1 c.c. of the invert sugar solution between 5 and 15·9 c.c., the reducing sugar content of the wine in grms. per litre.

Invert sugar solution used c.c.	0·0.	0·1.	0·2.	0·3.	0·4.	0·5.	0·6.	0·7.	0·8.	0·9.
5	2·08	2·14	2·19	2·24	2·29	2·34	2·40	2·45	2·51	2·56
6	2·61	2·67	2·72	2·77	2·83	2·88	2·93	2·98	3·04	3·09
7	3·15	3·20	3·26	3·31	3·36	3·42	3·47	3·53	3·58	3·63
8	3·69	3·74	3·80	3·85	3·90	3·96	4·01	4·06	4·12	4·17
9	4·22	4·28	4·33	4·38	4·44	4·49	4·55	4·60	4·66	4·71
10	4·76	4·82	4·87	4·93	4·98	5·03	5·09	5·15	5·20	5·26
11	5·31	5·37	5·42	5·48	5·54	5·59	5·65	5·70	5·76	5·82
12	5·87	5·93	5·99	6·05	6·10	6·16	6·22	6·28	6·33	6·39
13	6·45	6·50	6·56	6·62	6·67	6·73	6·78	6·84	6·89	6·95
14	7·00	7·06	7·12	7·18	7·24	7·30	7·36	7·42	7·48	7·54
15	7·60	7·66	7·72	7·78	7·84	7·90	7·95	8·01	8·07	8·12

T. H. P.

Determination of Lactic Acid in Wines. J. H. Fabre and E. Bremond. (*Ann. Falsificat.*, 1931, **24**, 474–477.)—Möslinger's method of determining lactic acid in wine, as modified by Bonifazi and Ferré (*Ann. Falsificat.*, 1928, **21**, 83), gives results (both with wines and with synthetic solutions similar in composition

to wines) accurate to within 0·32 grm. per litre. The procedure is as follows:—Twenty-five c.c. of the wine, in a 150 c.c. flask, are neutralised to phenolphthalein with saturated barium hydroxide solution and treated with 2·5 c.c. of 10 per cent. barium chloride solution. The volume is made up to 40 c.c. with water, and then to 150 c.c. with 96 per cent. (by vol.) alcohol. The whole is mixed, left at rest for 2 hours, and filtered; 100 c.c. of the filtrate are evaporated to dryness in a porcelain dish, and the residue is calcined. The alkalinity of the ash is determined by treatment with 10 c.c. of 0·2 *N* hydrochloric acid and titration with 0·2 *N* sodium hydroxide solution in presence of methyl orange. The result represents the sum of the lactic acid and the volatile acids. The latter may be determined directly by Mathieu's method, even in presence of considerable amounts of lactic acid.

T. H. P.

Determination of Lactic Acid in Wines. A. Michel. (*Ann. Falsificat.*, **1931, 24,** 471–474.)—When applied either to wines or to synthetic media, Bonifazi's method of determining lactic acid gives discordant results. The excess of barium chloride remaining in the filtrate is partly reduced during the subsequent calcination, and thus causes an increase in the alkalinity. With wines rich in potassium salts, these react with the barium chloride, yielding the more stable potassium chloride; for a definite content of lactic acid, such wines give results more accurate than those furnished by wines with less potassium salts. Moreover, it is not easy to neutralise exactly the free acids of the sample, and any excess of baryta, which dissolves readily in alcohol, renders the result too high. It is sometimes assumed that wine may contain dilactic acid, but experiment shows that this acid is very readily hydrolysed and that it does not exist in wine in any appreciable amount.

The following modification of Bonifazi's procedure is suggested:—Twenty c.c. of the wine, rendered alkaline to phenolphthalein with a slight excess of saturated baryta solution, are treated, in a 110 c.c. flask, with 2 c.c. of 10 per cent. barium chloride solution and with sufficient 95 per cent. (by vol.) alcohol to bring the volume to about 100 c.c. The reaction is adjusted, if necessary, to a pink colour, and the liquid is made up to the mark. After being mixed, the liquid is left at rest for 3 hours, in order that the barium succinate may be completely precipitated. The precipitate is removed by centrifuging or filtering, and the liquid is freed from the excess of baryta by means of a current of carbon dioxide or air. When it has settled, the barium carbonate is removed. From 80 c.c. of the remaining liquid, placed in a porcelain basin, the alcohol is carefully expelled on a water-bath; 2 c.c. of approximately *N* potassium sulphate solution are then added, and the evaporation is continued to dryness. The residue is calcined, and the alkalinity of the ash is determined by titration, using 0·2 *N* hydrochloric acid and 0·2 *N* sodium hydroxide. The volatile acids are determined separately, and their amount is subtracted from that of the acids, calculated from the result of the above titration, to obtain the lactic acid. Results obtained with a number of different wines are given.

T. H. P.

Fractional Titration of Wine Vinegar. Determination of Non-Volatile Acids. P. Hirsch and O. Delp. (*Z. Unters. Lebensm.*, 1931, **62,** 589–593.)—The sample (50 c.c.) is steam-distilled with 2 c.c. of 25 per cent. hydrochloric acid

until about 600 c.c. of distillate have been obtained, and the residue (about 50 c.c.) is filtered and diluted to 100 c.c. with the washings. Half of this is neutralised, firstly with 2 *N* and then with 0·1 *N* sodium hydroxide solution to phenolphthalein (*p*H 8·3), and transferred to a titration-colorimeter vessel (15·5 cm. × 3·5 cm.), provided with a compensating cell for the elimination of any colour originally present. The liquid is then titrated from *p*H 8·3 to *p*H 2·0 (*r* c.c.) with 0·25 *N* hydrochloric acid in the presence of 0·6 c.c. of a solution containing 100 mgrms. of thymol blue and 4·3 c.c. of 0·5 *N* sodium hydroxide solution per 100 c.c., the end-point being ascertained by comparison of the colour with that of a citrate buffer (Sörensen) of *p*H 2·0 containing, at the end of the titration, the same concentration of indicator as the sample. The influence of "free" acidity (*s* c.c.) is eliminated by a blank titration in the same way with 50 c.c. of water, and the required titration, corresponding with the sum of the tartaric, malic, lactic and succinic acids, is then given by $r - s$ (*cf.* Hirsch and Richter, *id.*, 1929, **58**, 439). Pure wine vinegars (9) contained 22·0 to 27·2 c.c. of 0·25 *N* non-volatile acids per 100 c.c. of sample; a "double" wine-vinegar (50 per cent. blend), 16·4; ordinary vinegar, 20 per cent. blend (6), 4·5 to 5·9; spirit vinegar (8), 0 to 0·2; 80 per cent. commercial "vinegar-essence" (14), 0 to 0·2; a mixture of pure wine and spirit vinegars (1 : 4), 4·75; and "wine vinegars" as sold (7), 0·7 to 5·6. J. G.

Fatty Acids of Chicken Fat and Other Edible Fats. J. Grossfeld. (*Z. Unters. Lebensm.*, 1931, **62**, 553–566.)—*Determination of lower volatile fatty acids.*—Five grms. of fat are saponified by heating over a naked flame in a 300-c.c. flask with 10 c.c. of glycerin and 2 c.c. of 50 per cent. potassium hydroxide solution, and a solution of the soap in 500 c.c. of water is shaken with 250 c.c. of a solution containing 15 grms. of crystalline magnesium sulphate. The mixture is made up to 1 litre, filtered on the following day, and 400 c.c. of filtrate are distilled in a 500-c.c. flask with 5 c.c. of phosphoric acid (sp. gr. 1·154), the first 300 c.c. of distillate being titrated with 0·1 *N* sodium hydroxide solution, with phenolphthalein as indicator. The amounts of lower fatty acids, calculated as percentage of (1) butyric, (2) caprylic and (3) nonylic acid, respectively, were:—Chicken fat, 0·03, 0·05, 0·06; goose fat, 0·01, 0·16, 0·18; beef fat, 0·11, 0·19, 0·21; mutton fat, 0·11, 0·19, 0·21; lard, 0; horse fat, 0·07, 0·11, 0·12; coconut oil, (1) 6·50, (2) 10·64; butter, (1) 5·56. Other analytical values for chicken fat were:—Saponification value, 195·2; iodine value (Hanus), 69·9 to 78·2; thiocyanogen value, 62·7 (ANALYST, 1929, **54**, 304); n_D^{40}, 1·4165. The lead salt method (*id.*, 1930, **55**, 451) gave the following percentages of solid fatty acids:—Chicken fat, 19·27 to 22·66 ± 1·01 (mean 21·36); goose fat, 27·83; horse fat, 29·30; lard, 38·10; beef fat, 40·73 and 53·05; mutton fat, 54·22; hardened arachis oil, 69·9. Saturated fatty acids higher than stearic acid were not detectable in chicken, goose, beef or mutton fats, or in lard. *Iso*-oleic acid occurs in quantities exceeding 1 per cent. only in beef fat (1 to 1·8 per cent.), in mutton fat (5·35 per cent.), and in hardened arachis oil (25·2 per cent.). In all cases the percentage of palmitic acid, calculated from the saponification value, was found to be higher (by 10 for chicken fat) than that calculated from the molecular weight of the solid fatty acids (*cf. id.*, 1930, **55**, 138; *Z. Unters. Lebensm.*,

1930, **60**, 64), and this is attributed to the presence of fatty acids with molecular weights below that of palmitic acid. The mean percentages of stearic, palmitic (+myristic and lauric), oleic (+vaccenic), and linolic acids (Kaufmann's method, *loc. cit.*), lower volatile acids and unsaponifiable matter, respectively, were:

	Stearic acid. Per Cent.	Palmitic (+myristic and lauric) acid. Per Cent.	Oleic acid +*iso*-oleic (vaccenic) acid. Per Cent.	Linolic acid. Per Cent.	Lower volatile acids. Per Cent.	Unsaponifiable matter. Per Cent.	Glycerol residue. Per Cent.
Chicken fat	7·1	18·4	52·7	17·0	—	0·28	4·4
,, ,,	8·5	17·5	52·2	17·1	0·1	—	4·4
Goose fat ..	10·1	20·0	46·8	18·4	0·2	0·14	4·4
Beef fat ..	41·7	18·5	33·0	2·3	0·0	0·08	4·5
Mutton fat ..	34·7	22·2	30·8	7·3	0·2	0·40	4·5
Lard ..	18·7	26·3	40·4	10·2	—	0·11	4·5
Horse fat ..	9·0	27·3	47·6	11·5	0·1	0·29	4·4

A purchased sample of cubes for the preparation of "chicken broth" contained 12·22 per cent. of fat, mainly hardened arachis oil. The Carr-Price reaction for vitamin *A* (*Biochem. J.*, 1926, **20**, 497; *cf.* Cocking and Price, ANALYST, 1926, **51**, 529) gave with 1 grm. of chicken-fat a light blue colour, turning red and producing eventually dark violet flocks, whilst the other fats gave a dark brown or red-brown colour. The colour of the melted fat may be measured by comparison with solutions of potassium dichromate; the colouring matter is partly bleached by the action of nitrous acid or by exposure for 2 hours to ultra-violet light. The colour of chicken fat matched *N*/80 potassium dichromate solution before, and *N*/1280 after the exposure. Experiments, described in detail, indicated the colouring matter of the fat to be closely related to that of hens' egg yolk.

J. G.

Melting and Solidification Points of Hydrogenated Waxes and Oils and of their Fatty Acids. S. Ueno, G. Inagaki and H. Tsuchikawa. (*J. Soc. Chem. Ind. Japan*, 1931, **34**, 445B.)—Little difference was found between the melting and solidification points of five hardened waxes (type unspecified) with iodine values of 4·0 to 8·5. The m.pt. of their fatty acids, however, was 1 to 2° C. higher than the solidif. pt. Four hardened herring oils (iodine values, 2·9 to 4·3) had m.pts. 55° to 57° C., and solidif. pts. of 50° to 50·6° C. The m.pts. and solidif. pts. of the fatty acids showed little difference at about 54 to 56° and 54 to 55° C., respectively. The m. pt. of a hardened sardine oil of iodine value 2·9 was found to be 55·0° to 56·5° C., whilst the solidif. pt. of its fatty acids was 53·5° C. For another sample, with iodine value 18·0, these values were 51·6° to 52·0° C. and 49·5° C., respectively.

R. F. I.

Fatty Acids and Glycerides of Solid Seed Fats. I. Composition of the Seed Fats of *Allanblackia Stuhlmannii*, *Pentadesma Butyracea*, *Butyrospermum Parkii* (Shea), and *Vateria Indica* (Dhupa). T. P. Hilditch and S. A. Saletore. (*J. Soc. Chem. Ind.*, 1931, **50**, 468–472T.)—The objects of the examination of seed fats are to collect sufficient data to establish ultimately the limits within which specific mixtures of fatty acids are characteristic of botanical families, and to

obtain further evidence on their glyceride structure and the even distribution of the component acids through the glyceride molecules. *Allanblackia Stuhlmannii* (from the East African Agricultural Research Station, Amani).—The whole seeds yielded 50 per cent. of fat, having m. pt., 40·0° C.; setting point, 35·5° C.; saponification equivalent, 293·2; iodine value, 39·4; acid value, 8·0; unsaponifiable matter, 0·55 per cent. The mixed fatty acids had the mean molecular weight 280·2; iodine value, 41·4; and setting pt., 59·9° C. The mixed fatty acids were submitted to the usual procedure for the separation of solid and liquid acids and fractionation of the corresponding methyl esters, and were found to have the following composition:—Palmitic, 3·1; stearic, 52·6; oleic, 44·1; and linolic acid, 0·2 per cent.; showing 1·25 mols. of saturated acids per mol. of unsaturated acid in the whole seed fat. Oxidation of the fat with potassium permanganate in acetone solution showed that the fully-saturated glycerides in the original fat did not exceed 1·5 per cent., and that the proportion of palmitic acid in the fully saturated components was much higher than in the fat as a whole. The possible amounts of the various mixed glycerides must lie between mono-oleo-disaturated glycerides 63·5 to 82; di-oleo-mono-saturated glycerides 36·5 to nil; and tri-olein nil to 18 per cent., with probable approximation to the first figures.

Pentadesma Butyracea (from Sierra Leone).—The kernels yielded 41 per cent. of a fat having m. pt., 33·5 to 34° C.; setting point, 35·4° C.; saponification equivalent, 294·7; iodine value, 42·9; acid value, 12·5; and unsaponifiable matter, 0·5 per cent. The mean molecular weight of the fatty acids was 281·6; iodine value, 44·5; and setting point, 57·7° C. The fatty acids were found to consist of palmitic, 5·4; stearic, 46·1; and oleic acid 48·59 per cent., showing 1·1 mol. of saturated acid per mol. of oleic acid. The limiting figures for the glycerides worked out at mono-oleo-disaturated, 50 to 75 per cent.; di-oleo-mono-saturated, 50 to nil; and tri-olein, nil to 25 per cent. The distribution of the fatty acids among the glycerol molecules is very largely, but not wholly, of the "even" character usual in seed fats.

Butyrospermum (Bassia) *Parkii,* Fam. *Sapotaceae* (Shea nuts).—Since the conclusions of Bougault and Schuster (*Compt. rend.*, 1931, **193**, 362) are not in agreement with those of the present paper the experimental data are given in some detail. The refined shea butter had the saponification equivalent 314·2; iodine value, 57·3; acid value, 2·1; unsaponifiable matter, 9·5 per cent.; mean molecular weight of fatty acids and unsaponifiable matter, 293·2; iodine value, 57·2; setting point, 51·0° C. The approximate percentages of fatty acids were: Palmitic, 8·5; stearic, 36; oleic, 50; and linolic, 5·5 per cent. The fat contained about 2 per cent. of fully-saturated glycerides with palmitic and stearic in about equal molecular proportions, and the limits for the glycerides were mono-oleo-disaturated 30·5 to 65; di-oleo-mono saturated 69·5–nil, and linolin nil to 35 per cent. (probably nearer the first figures).

Vateria indica (dhupa kernels), *Dipterocarpaceae* (from Bangalore).—The fat had the saponification equivalent 303·5; iodine value, 42·8; acid value, 8·8; and the mean equivalent of the mixed acids was 286·1; iodine value, 45. The component fatty acids were palmitic, 10; stearic, 39; arachidic, 3; and oleic, 48 per cent. The quantity of fat was not sufficient to allow of investigation of the glyceride structure.

The results of the investigation of the component fatty acids of seed fats by modern methods show:

Family	No. of species examined.	Stearic greater than palmitic.	Stearic less than palmitic.
Guttiferae	4	3	1
Sapotaceae	2	2	0
Dipterocarpaceae ..	2	2	0

The analyses of these fats confirm the "evenly distributed" nature of the fatty acids among the glyceride molecules, and the concentration of the palmitic acid in the fully saturated portions is again noticeable. D. G. H.

Determination of Caffeine in Coffee Decoctions and Coffee Extracts. A. Bonn and Ch. Desgrez. (*Ann. Falsificat.*, 1931, **24**, 546–547.)—The following method for the determination of caffeine in infusions and extracts of coffee (also applicable to the determination of added caffeine in wines) is based on the French (1908) Codex method for the determination of caffeine in extracts of cola. Between 75 and 100 c.c. of the liquid are evaporated almost to dryness, the residue is mixed with 15 grms. of recently calcined magnesia, and, after 1 hour, the mixture is transferred to a dry flask and 125 c.c. of chloroform (dried over copper sulphate) are added, and the flask is counterpoised. The mixture is boiled beneath a reflux condenser for 45 minutes, the counterpoise then checked, the liquid filtered, and the volume of the filtrate is noted. The chloroform is distilled off, and the slightly tinted residue is taken up with a few c.c. of chloroform, and finally with 10 c.c. of 5 per cent. hydrochloric acid. A sufficient quantity of 5 per cent. silicotungstic acid to effect complete precipitation is added (about 25 to 30 drops per 10 mgrms. of hydrated caffeine), the precipitate is dissolved by warming, and, after 24 hours, it will have re-formed in a convenient state for filtration. It is washed with 5 per cent. hydrochloric acid, dried, calcined, and weighed; one grm. of the resulting silicotungstic oxide corresponds with 0·2236 grm. of hydrated caffeine. D. G. H.

Determination and Separation of Saligenin, Salicylic Acid, and Salicylaldehyde. R. Berg, W. Grimmer and A. Müller. (*Chem. Ztg.*, 1931, **55**, 975.)—When an ethereal solution of these three compounds is extracted with a measured excess of standard sodium bicarbonate solution, this dissolves all the salicylic acid as sodium salicylate and also a small quantity of the salicylaldehyde, whilst the whole of the saligenin and most of the aldehyde remain in solution in the ether. The unused excess of bicarbonate may be determined by titration with mineral acid, the small amount of salicylaldehyde present serving as indicator. The aldehyde may then be converted into its oxime, and this precipitated in acetic acid solution buffered with sodium acetate and filtered off. After evaporation of the ether from the residual solution, the saligenin may be determined gravimetrically. The procedure is as follows:

The ethereal solution of the three compounds is shaken repeatedly with measured volumes of 0·05 *N* sodium bicarbonate solution; for 0·15 to 0·2 grm. of salicylic acid, four treatments with 10 c.c.-portions of the bicarbonate solution, followed by three treatments with 5-c.c. portions of water, are sufficient. The

final washing water must be coloured yellow immediately by a drop of 0·05 *N* sodium hydroxide solution; if not, extraction with further quantities of bicarbonate must be carried out. The combined pale-yellow extracts are treated with a measured volume of 0·05 *N* hydrochloric or sulphuric acid—a few c.c. more than are required to decolorise the liquid. The solution is heated to expel the carbon dioxide completely, cooled, and titrated at once with 0·05 *N* sodium hydroxide solution (as free from carbon dioxide as possible) until a persistent yellow coloration appears. The remaining ethereal solution is carefully concentrated, and the residue is treated with water containing a few drops of dilute sodium hydroxide solution. After expulsion of the ether by distillation, the faintly alkaline liquid is neutralised, and any turbidity is removed by slight addition of alcohol. The solution (about 20 to 25 c.c.) is transferred quantitatively to a stoppered bottle of about 100 c.c. capacity and heated for 30 to 40 minutes in a water-bath at 45° to 50° C. with a solution of 0·2 grm. of hydroxylamine hydrochloride previously made just pink to phenolphthalein by addition of alkali; the end of the reaction is recognised by complete decolorisation of the yellow solution. The product of the reaction is cooled, acidified, and extracted with ether in a separating funnel, the salicylaldoxime and saligenin being then removed from the ethereal solution by shaking this with three or four 5 c.c. quantities of *N* sodium hydroxide solution. The combined alkaline solutions are neutralised or made faintly acid with a mineral acid and treated with a solution of 0·3 grm. of sodium acetate (neutral or very slightly alkaline to phenolphthalein) and 3 c.c. of 3 per cent. copper sulphate solution. The micro-crystalline copper-salicylaldoxime compound (sometimes mixed with cuprous salt of the excess of precipitant, resulting from reduction of the hydroxylamine) is collected on a fine-pored filter. The saligen is completely extracted from the filtrate by shaking this with ether, and the ethereal solution is dried over anhydrous sodium sulphate and freed from ether by distillation. The residue is dried in a vacuum, and the resulting pure crystalline saligenin is weighed. T. H. P.

Biochemical

Kinetics of Milk Catalase on Heating. A. I. Burstein and F. S. Frum. (*Z. Unters. Lebensm.*, 1931, **62**, 489–500.)—Morgulis's method for determining the catalytic activity of milk (*J. Biol. Chem.*, 1921, **47**, 341) is improved by controlling the temperature of the mixture of milk and hydrogen peroxide solution by means of a thermometer dipping into the mixture itself and not into the bath surrounding the containing flask. The test is made at 17° C., with 60 c.c. of milk, 18 c.c. of a mixed phosphate buffer solution of *p*H 6·5, and 15 c.c. of 1 per cent. aqueous hydrogen peroxide solution. The method gives results more accurate than those yielded by the so-called "catalasers" of Lobeck, Funke, and others.

Under the above conditions, fresh, healthy milk with acidity (according to Thörner) not exceeding 20, yields 3·5 to 14·5 c.c. of oxygen. When milk is heated, the catalase undergoes gradual inactivation, this effect being influenced more by the temperature than by the duration of the heating. The acidity of milk exerts a protective influence on the catalase during heating. The enzyme is irrecoverably inactivated at a temperature of 90° to 92° C., maintained for 20 to 30 minutes,

but if the enzyme is not completely inactivated, the milk improves in catalytic activity when kept. When tested against a control sample, previously heated at 100° C. for 30 minutes, properly pasteurised milk should exhibit catalytic activity, but should not yield more than 8 c.c. of oxygen shortly after pasteurisation. Absence of catalase indicates that the milk had been heated to 90° to 92° C. at least, whilst evolution of more than 8 c.c. of oxygen shows either that the temperature requisite for sterilisation (60° C. at the minimum) had not been maintained for 30 minutes, or that the milk pasteurised was unsound or not fresh.

If pasteurised milk is kept for a few hours, especially if under non-sterile conditions and at comparatively high temperatures, the catalase content increases and may even surpass the maximum value found with freshly-pasteurised milk. Boiled or properly sterilised milk should develop no catalytic activity when stored under any conditions and for any period. T. H. P.

Influence of Sunlight on Milk. H. R. Whitehead. (*Biochem. J.*, 1931, **25**, 1647–1652.)—The author (*Biochem. J.*, 1930, **24**, 579; ANALYST, 1930, **55**, 594) showed that sunlight caused a decolorisation of methylene blue in milk independently of bacteria, and that the reaction was accompanied by an oxidation of some portion of the milk-fat. Other workers have shown that whole milk exposed to sunlight develops a "cardboard" or tallowy flavour, due to oxidation of the milk-fat. It is probable that the presence of methylene blue in milk exposed to sunlight merely results in a visual indication of the intensity with which the oxidation of the fat is taking place. The author has observed that milk samples, exposed to sunlight with or without methylene blue, develop the tallowy flavour, but neither the tallowy flavour nor the reduction of methylene blue occurs in milk from which the fat has been removed, and, therefore, it is almost certain that the two phenomena are dependent upon a single oxidation-reduction reaction. This reaction has been given a more detailed examination. The potentiometric method of Clark *et al.* (*U.S. Pub. Health Service, Hyg. Lab. Bull.*, 1928, No. 151) was applied. The results show that the oxidation of fat in whole milk under the influence of sunlight causes the development of a reducing potential, which can be detected either by its effect on methylene blue or by measurement electrometrically. The fact that a fall in the E_h value occurs in the absence of methylene blue indicates that the dye is not essential to the reaction, and that there must be some reversible system in milk capable of acting as a hydrogen acceptor. The potential developed is poorly poised and of small capacity; hence, experimental error in the measurement of potentials is great. Heated milk and raw milk give similar results. Separated milk, in many cases, undergoes no change under the influence of sunlight, but some samples show a fall in potential which is not at present satisfactorily explained. When such a fall in potential occurs in separated milk there is a subsequent drift to more positive potentials. This suggests the presence in milk of a slowly acting reversible system which tends to maintain the E_h at a value between +0·2 and +0·3v. Most milk samples, in the absence of influences such as sunlight and bacteria, attain equilibrium with a gold electrode at about this value of E_h. It has not been found possible to reproduce the effect of sunlight by the use of either ultra-violet radiation or radiation from electric lamps. The

agent inducing oxidation of fat in milk is probably some portion of visible light of which there is less in the radiation of the mercury vapour lamp than in sunlight. In certain cases (*e.g.* whole milk undergoing rapid changes in sunlight) the potential on the electrode seems to lag in its indication of the conditions in the medium. When the E_h falls more gradually or the medium is more nearly homogeneous, the potential on the electrode gives a more accurate indication of the conditions in the medium from moment to moment. Therefore, under certain conditions, a dye may give a truer indication of the oxidation-reduction potential of a solution than the potential on an electrode. P. H. P.

Method for the Direct Determination of Urea in Urine. S. W. Cole. (*Biochem. J.*, 1931, **25**, 1653–1655.)—A modification of the method of Marshall (*J. Biol. Chem.*, 1913, **14**, 483; ANALYST, 1914, **39**, 39) is described by which the determination of urea in urine can be completed in 20 minutes; it is accurate to within 2 per cent. A stronger enzyme preparation is used, and the fluid is maintained under optimal conditions of reaction. The solutions required are:—(*a*) 0·1 *N* hydrochloric acid, in two burettes; (*b*) mercuric chloride, 0·5 per cent. made up to 100 c.c.; (*c*) ammonium chloride, 10 per cent.; (*d*) phenolphthalein, a saturated solution in 50 per cent. alcohol; (*e*) methyl red, 0·02 per cent. in 60 per cent. alcohol; (*f*) urease solution, made from "Arlco" Jack Bean Meal. Four grms. of the meal are rubbed in a mortar into a cream with 10 c.c. of distilled water, washed into a beaker with more water until 100 c.c. have been added, stirred, left for some minutes, and poured off from the deposit of starch and other insoluble material. This preparation is simply made, but gives a precipitate at the final end-point of the titration, which does not interfere with the accuracy. For an almost clear solution, a 4 per cent. suspension of the meal is made as described above, with the exception that the last 50 c.c. of water are warmed to about 60° C. before being added. The whole is treated with 4 c.c. of 0·1 *N* hydrochloric acid, mixed, and filtered through a pleated paper. The slight precipitate, which is gradually deposited, should not be filtered off. The method of determination is as follows:—To 3 c.c. of filtered urine in each of two similar 100-c.c. beakers, labelled A and B, are added about 20 c.c. of distilled water at 60° C. and 5 drops of the phenolphthalein solution. Then 10 c.c. of the enzyme preparation are added to A. The mixture in A is titrated with 0·1 *N* hydrochloric acid, at such a rate as just to discharge the red colour; this prevents loss of ammonia, and maintains a reaction of about *p*H 8·2. It is not generally necessary to add any acid after about 5 minutes. While A is left standing for about 12 or 15 minutes, 1 c.c. of the mercuric chloride solution and 1 c.c. of the ammonium chloride solution are placed in B, mixed, and 10 c.c. of the enzyme preparation and 20 drops of the methyl red are added. In this case the urease cannot act in the presence of the mercury. From a second burette 0·1 *N* hydrochloric acid is added until a full red colour is obtained, and enough water to make the volume slightly greater than that in A. The fluid in A is then treated with 1 c.c. of the mercuric chloride solution and 20 drops of methyl red, and titrated with hydrochloric acid until the colours of the fluids in the two beakers match, the volumes being kept constant by the addition of water to one or the other. As 1 c.c. of 0·1 *N* hydrochloric acid is equivalent to

3 mgrms. of urea, the number of c.c. of the acid added to A, less that added to B, gives the urea in grms. per litre. P. H. P.

Colorimetric Determination of Uric Acid in Urine. H. B. Salt. *Biochem. J.*, 1931, **25**, 1720–1723.)—Although one of the difficulties of the determination of uric acid in blood, namely, the development of turbidity in the final solution used for colorimetric comparison, has been entirely overcome, the method for uric acid in urine has not been studied, so far as is known, with this aim in view. Therefore, the method of Folin (*Laboratory Manual of Biological Chemistry*, 1923, p. 141) for the determination of uric acid in urine has now been investigated, and a modification is described, which is easily carried out in routine practice, yields results strictly comparable with those obtained by Folin's original technique, and is free from the objection of turbidity in the final colours. Folin's method depends upon the reduction of phospho-18-tungstic acid by uric acid in the presence of a large excess of sodium carbonate; sodium cyanide is also present, and the reaction proceeds at room temperature. The improved uric acid reagents have been substituted, and the conditions of reaction modified. The following reagents are required for the new method:—(1) Uric acid reagent of Folin and Marenzi (*J. Biol. Chem.*, 1929, **83**, 109); (2) uric acid standard solution of Folin (*J. Biol. Chem.*, 1930, **86**, 179), containing 1 mgrm. uric acid per c.c. This is diluted ten times with water alone, to prepare the working standard when required; (3) cyanide-urea reagent of Folin (1930); (4) acid silver lactate reagent prepared by the method of Folin (*J. Biol. Chem.*, 1922, **54**, 153; ANALYST, 1922, **47**, 309); the solution is always filtered immediately before use; (5) sodium carbonate solution containing 20 grms. of anhydrous sodium carbonate per 100 c.c. of solution. This is referred to as "20 per cent. sodium carbonate." Suitable dilutions are made, *e.g.* "10 per cent. sodium carbonate" is a 1 : 1 dilution. The method recommended is as follows:—To 1 c.c. of urine (or more if the uric acid content is low) in a centrifuge tube are added 3 c.c. of water and 3 c.c. of acid silver lactate solution. The whole is mixed, left in the dark for a few minutes, and then centrifuged. The supernatant liquid is discarded. The precipitate is dissolved in 5 c.c. of cyanide and urea reagent and transferred quantitatively to a 100 c.c. measuring flask, and two successive portions of 10 c.c. of 10 per cent. sodium carbonate solution, and finally 5 c.c. of water, are added. For the standard, 5 c.c. of standard uric acid solution (containing 0·5 mgrm. of uric acid), 5 c.c. of cyanide and urea reagent and 20 c.c. of 10 per cent. sodium carbonate solution are transferred to a 100-c.c. measuring flask. To each flask are then added 5 c.c. of uric acid reagent, and the contents are mixed, and allowed to stand for 5 minutes. The contents of each are diluted to volume, mixed, and compared in the colorimeter. P. H. P.

Amounts of Aluminium in Plants, especially Edible Plants. G. Bertrand and G. Levy. (*Bull. Soc. Chim.*, 1931, **49-50**, 1417–1425.)—Aluminium was found to be present in all the phanerogams examined, varying from a tenth of a mgrm. to several dgrms. per kilo. of dry material, and the results showed that the absorption is most rapid during the early life of plants. Edible cultivated roots appear to contain considerably less aluminium than wild ones (*e.g.* forage beet 6 mgrms. per kilo. of dry material, young carrot 30 mgrms., dandelion 120 mgrms.),

and the amounts present in tubers are of the same order as in the edible roots. The same is true of most fruits, but bananas and oranges contain very little aluminium (6–7 mgrms. for oranges, 1·4 mgrm. per kilo. in the edible part of the bananas). Seeds are also poor in aluminium; *e.g.* maize 0·2 mgrm., and white rice 1·4, but coffee contained 46·2 mgrms. per kilo. It is in leaves that the highest proportions are usually met with, *e.g.* rhubarb 166 mgrms., Ceylon tea 465, plantain 60 mgrms. per kilo. Etiolated leaves contain hardly any aluminium; for example, the outside leaves of a cabbage contained 232 mgrms., and those inside 8 mgrms. per kilo. D. G. H.

Vitamin *B* Content of Commercial Liver Extracts and Stomach Preparations. E. Gilroy. (*Lancet*, 1931, **221**, 1093–1098.)—During the past year eleven commercial liver extracts and four stomach preparations, as used in the treatment of pernicious anaemia, have been tested for their ability to promote normal growth in young rats on a diet deficient in all water-soluble vitamins. Nine of the liver extracts and three of the stomach preparations gave excellent growth. (A twelfth liver extract subsequently tested gave good growth.) From certain preliminary experiments it appears that a liver fraction for intravenous injection does not contain vitamin B_1, the antineuritic factor. The equivalent of 16 grms. of fresh liver was found to be an efficient dose; half this amount induced fair, but subnormal, growth. Standardisation of the first extract to be tested showed that 1 c.c. (equivalent to 16 grms. of fresh liver) was approximately equivalent to 1 grm. of acetone-extracted wheat germ. The addition of a fraction soluble in 92 per cent. alcohol (discarded in the process of manufacture) to the two extracts which failed to support normal growth, caused an immediate resumption of rapid growth; however, an alcohol-soluble fraction, rejected from the other extract, failed to have any effect. In the two extracts referred to, the amount of the antineuritic factor was considered to be negligible. Therefore, the conclusion is justified that liver and stomach preparations, as used in the treatment of pernicious anaemia, are rich in vitamins B_1 and B_2, and only in exceptional cases does the process of manufacture exclude the first factor of the complex; it is seldom actually destroyed, as the method of preparation is not liable to cause any inactivation. It is the more remarkable that vitamin B_2 is not destroyed, or, at any rate, partially removed, in the process of manufacture, since this always involves extraction, or washing, with alcohol of a strength which should cause considerable loss of B_2. Differences in *p*H are known to modify the sensitivity of B_2 to alcohol, but it seems unlikely that commercial liver-extract would be a sufficiently acid medium to protect the vitamin completely, and it must be assumed that some other factor is responsible for the survival of vitamin B_2 in proprietary liver extracts. In a small series of experiments upon mice, evidence was obtained that a dose of liver extract sufficient for maintenance in the normal, unmated, adult animal is inadequate during pregnancy. It appears possible that premature births, and other morbid phenomena, may be associated with a relative deficiency of vitamin *B*. The significance of the antineuritic factor of the vitamin *B* complex in the aetiology of certain types of pernicious anaemia, and in the treatment of such conditions, is discussed, with reference to recent clinical observations. It is appreciated that

the "pernicious anaemia" of pregnancy, which has been shown to respond to treatment with marmite, may prove to be distinct from typical Addison's anaemia, and that the latter may prove entirely resistant to similar forms of treatment.

P. H. P.

Colour Reactions of Liver Oil. R. T. A. Mees. (*Chem. Weekblad*, 1931, **28**, 694–696.)—The author objects to the Carr-Price test (*Biochem. J.*, 1926, **20**, 497; *cf.* Cocking and Price, ANALYST, 1926, **56**, 529), principally on the ground that the colour is not sufficiently stable. He found that 5 c.c. of a 10 per cent. solution of antimony trichloride in benzene give a colour with 0·5 c.c. of oil which increases to a maximum after 2 to 3 hours. It is less sensitive than the Carr–Price colour reaction, however, though comparative tests on cod-liver and palm oils gave parallel results for vitamin *A* content by the two methods; for example, when the Carr–Price colours were 13·5 B (blue) and 14 B + 4 Y (yellow), respectively, the new method gave (11·9 B + 12·2 Y) and (2B + 55Y), respectively, the preponderance of yellow in the latter case being due probably to the presence of carotene. Solutions of the reagent in trichloroethylene or carbon tetrachloride gave colours similar to that of the Carr–Price test, though developing less rapidly in the latter case, *e.g.* to (10B + 35Y) with a liver oil having a Carr–Price value of 12·5 B; amyl acetate and chlorobenzene also produced more stable but weaker colorations, whilst with toluene and xylene a greenish tint was obtained. A 20 per cent. solution of aluminium trichloride in ether gave in 15 minutes with the same sample a colour matching 50 red.

J. G.

Water Analysis

Titration of the Alkali Metals in Water. J. Tillmans and E. Neu. (*Z. Unters. Lebensm.*, 1931, **62**, 593–596.)—The sample (50 to 1000 c.c., according to the alkali metal content) is evaporated with 10 drops of sulphuric acid in a platinum dish, and the residue is gently ignited to remove organic matter and excess of acid. A boiling solution of the residual sulphates is precipitated with a slight excess of barium hydroxide solution, and the mixture is then cooled, made up to a definite volume and filtered, and carbon dioxide is bubbled through an aliquot portion of the filtrate (containing phenolphthalein) until the red colour has disappeared. The colour is restored by evaporation of the mixture, and the precipitation of the alkaline earth carbonates is completed by addition to the boiling liquid, drop by drop, of exactly 20 c.c. of 0·1 *N* sodium carbonate solution. The mixture is filtered when cold, the precipitate is washed with 25 c.c. of cold water free from carbon dioxide, and the alkali metal carbonates are titrated with 0·1 *N* hydrochloric acid to methyl orange. If allowance is made for the amount of sodium carbonate solution required in the last stage, the titration gives the sum of the equivalents of the sodium and potassium salts present. The result is calculated as sodium chloride, and, if no potassium is present, the error is ±0·3 mgrm. for 8 to 88 mgrms. of sodium chloride (tested for an "artificial" water containing the usual salts). Satisfactory agreement with the gravimetric method was obtained for natural waters containing 3 to 3570 mgrms. of sodium chloride, and having low potassium chloride contents.

J. G.

Organic Analysis

Detection and Determination of Methyl Chloride in Air and Foods. M. J. Martinek and W. C. Marti. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 408–410.)—The most efficient field test for leaks of gas containing methyl chloride is carried out by means of a small alcohol lamp with a cone of copper gauze above the wick. In the presence of organic halides the pale blue flame burns bluish-green. The lower limit of inflammability is 8·1 per cent. by volume of the gas in air, and the test is sensitive to 1 part in 100,000. A combustion method is used for laboratory tests. The gas is passed by suction through a quartz combustion tube heated to 1000° C., and then through a bottle containing silver nitrate. The test is sensitive to about 50 parts of methyl chloride per million parts of air. The combustion method is also used for the quantitative determination. The tube is 4 feet long, with an internal diameter of $\frac{1}{4}$ inch, and is heated electrically. The gas to be analysed is measured from a micro-burette or from a 200-c.c. Thoerner gas-sampling bottle, and passed into a dilution chamber, where it is mixed with dry, halogen-free air, and during the combustion the gases are drawn through the tube at the rate of 0·5 cb. feet per hour; the combustion takes one hour. The gases pass into the absorption solutions through tubes containing sintered glass filters, with pores measuring 100–120 microns (No. G1), which break up the gas into small bubbles. The best absorbent was found to be alkaline sodium arsenite, made by dissolving 0·2 grm. of arsenious oxide in 100 c.c. of a 1·0 per cent. solution of sodium carbonate; of this, 20 c.c. are used in each of the two absorption bottles. After the combustion is complete the bottles are removed, and the contents are washed into a 100-c.c. measuring flask containing 5 c.c. of nitric acid (3:1), 25 c.c. of 0·1 *N* silver nitrate solution are added, and the contents are diluted to 100 c.c. After shaking and allowing the contents of the flask to settle, 25 c.c. of the filtered solution are titrated with 0·05 *N* potassium thiocyanate solution, using a 5-c.c. micro-burette capable of delivering drops of the order of 0·01 c.c., a crystal of ferric ammonium sulphate being used as indicator. The error of determination was ±0·5 per cent. For the determination of methyl chloride in foodstuffs or in biological liquids, the material is heated in a flask over a water-bath, and halogen-free air is drawn through the warmed sample at the rate of $\frac{1}{4}$ cb. ft. per hour, directly into the combustion tube. The hydrochloric acid or chlorine in the foodstuff is determined by passing the hot air from the tube directly into the arsenite solution. J. W. B.

New Colour Reaction of Formaldehyde and Ketones with Sodium Nitroprusside and Hydroxylamine. P. Pratesi. (*Giorn. Chim. Ind. Appl.*, 1931, **13**, 513.)—Sodium nitroprusside solution (not too dilute) is treated with crystals of a hydroxylamine salt and a few drops of 40 per cent. formaldehyde solution, and the liquid is then made alkaline by addition of approximately 2 *N* sodium hydroxide solution. The first drops of the alkali, which liberate the hydroxylamine, produce a yellow coloration, this disappearing when the liquid is mixed. Further addition of the alkali gives an intense, dark, violet-red colour, which persists for days, but immediately changes to yellow if a large excess of alkali

is introduced. If sufficient formaldehyde is present, slight evolution of gas occurs. Aliphatic ketones, such as acetone, methyl-ethyl-ketone, and methyl-propyl-ketone, give a similar, but less stable, coloration. The coloured products of these reactions are precipitated from their aqueous solutions by ethyl alcohol. T. H. P.

Quantitative Determination of Acetone in Mixtures of Other Organic Solvents by means of Hydroxylamine Hydrochloride. M. Krajčinović. (*Chem. Ztg.*, 1931, **55**, 894–895.)—Messinger's iodimetric method for the determination of acetone gives high results in the presence of substances (*e.g.* ethyl alcohol or acetate, or impurities occurring in benzol) which react with iodine in alkaline solutions. The author, therefore, recommends the addition of a known amount of sample (*e.g.* lacquer solvent) to an excess (1 to 2 grms.) of hydroxylamine hydrochloride dissolved in a little water containing 2 drops of methyl orange solution in a 200 c.c. flask, and titration with 0·1 *N* sodium hydroxide solution of the hydrochloric acid liberated according to the equation, $(CH_3)_2CO + NH_2OH.HCl = (CH_3)_2C:NOH + H_2O + HCl$; then, acetone = 0·0058 × c.c. used. Since the reagent decomposes on keeping, especially in the light, it should first be tested for free hydrochloric acid, and neutralised, if necessary. The error for 0·23 to 9 grms. of acetone per 100 grms. in the presence of the above solvents is − 0·5 (with benzol) to +1·2 mgrms. J. G.

Quantitative Analysis of Dyestuffs. S. R. Trotman and T. B. Frearson. (*J. Soc. Dyers and Color.*, 1931, **47**, 344.)—New methods for the quantitative analysis of dyestuffs have been based on their precipitation by solutions of salts of alkaloids. Direct dyestuffs are completely precipitated by salts of quinine, cinchonine, quinidine and strychnine. They may thus be separated from acid dyestuffs, some of which are not so precipitated. The sodium salt of α-naphthalenesulphonic acid may be completely precipitated by adding an excess of cinchonine sulphate. The precipitate has a composition corresponding with the formula $(RSO_3H)_2(C_{19}H_{22}N_2O)_2$. Found:—Sulphur, 6·17; alkaloid, 58·7 per cent. Calculated: Sulphur, 6·37; alkaloid, 58·68 per cent. The alkaloid was determined by treating the salt with alkali and weighing the liberated alkaloid after extraction with chloroform. Chrysophenine, diamine sky blue, many chorazol colours, titan yellow, Congo red, etc., etc., may be determined in a similar manner. Primuline may also be determined by extraction with a mixture of toluene and absolute alcohol. After-treatment of cotton fabric with an alkaloid did not affect its fastness to light and washing. It is suggested, however, that artificial silk stockings treated with quinine acetate might act as a protective against bites by gnats and mosquitos.

Some acid dyestuffs are completely precipitated by alkaloid—alkali blue 5B, neutral red, cardinal red, milling scarlet, etc. Those which require the use of a strong acid are, in many cases, not precipitated, or, if so, the precipitate is soluble in dilute acetic acid, whereas that given by direct dyestuffs is insoluble—acid magenta, croceine scarlet, and some neolan colours.

Method for separating Direct and Acid Dyestuffs.—The dyestuff solution is well diluted, made acid with acetic acid, and heated to boiling. Excess of cinchonine sulphate solution is added, drop by drop, and the precipitate is collected on a

Gooch crucible. The precipitate is dissolved in boiling water, cooled, re-precipitated as before, filtered off, and washed. The combined filtrates, containing all the acid dyestuffs, are acidified with sulphuric acid, and the dyestuffs are deposited on wool. The precipitate is dissolved, the solution is made alkaline, and the direct dyestuffs are deposited on mercerised cotton. Certain acid dyestuffs may be separated from each other by the same technique, *e.g.* polar red is precipitated, whilst erio anthracene blue 3G is not.

This precipitation of dyestuffs enables inorganic sulphates and chlorides to be readily determined in the filtrate by the usual inorganic methods. It is tentatively suggested that basic dyestuffs may be precipitated by silicotungstic acid in the presence of a little hydrochloric acid. The precipitate, which is insoluble even in boiling water, is filtered off, washed, dried, weighed, and ignited. The residue is $SiO_2.12WO_3$, and from its weight the quantity of basic dyestuff may be calculated.

R. F. I.

Detection of Woody Plant Membranes with Phloroglucinol and Hydrochloric Acid. W. Plahl. (*Z. Unters. Lebensm.*, 1931, **62**, 603–606.)—As the result of a number of experiments carried out under different conditions, the following procedure is recommended:—The specimen is freed from fat in the usual way and extracted in warm water or in 50 to 60 per cent. alcohol to dissolve cell-juices; starch need not be removed. The section is then treated with 2 drops of a reagent consisting of equal volumes of a 2·5 per cent. solution of phloroglucinol in 96 per cent. alcohol and an aqueous solution of chloral hydrate (5 : 2), to which mixture 4 per cent. of hydrochloric acid (sp. gr. 1·124 to 1·126) is added. The test is best carried out in a watch-glass, any excess of reagent being removed by a strip of filter-paper before the specimen is transferred to the microscope slide. The colour is visible after 5 minutes; it reaches its maximum after 15 minutes, and is stable for a day.

J. G.

Sandalwood Substitutes. K. A. Chowdhury. (*Indian Forester*, Sept., 1931; *Perf. Ess. Oil Record*, 1931, **22**, 332–333.)—In order to distinguish true sandalwood (*Santalum album*, Linn.) from kalamet wood (*Mansonia Gagei*, Drum.), a detailed examination of each wood is reported. True sandalwood has white sapwood often tinged with yellow, and brownish-grey heartwood streaked with alternate light and dark bands. The wood has the following characteristics:—Oily and smooth; a strong odour; weight per cb. ft. approximately 60 lbs.; moderately hard; almost straight-grained; texture, very fine and even. The growth rings are fairly distinct, marked by bands of denser fibrous tissue (7·14 per inch). The appearance of the pores is shown in Fig. 1, and the rays have an irregular arrangement, as seen tangentially (Fig. 3).

Kalamet wood has dull white sapwood, blackish-grey heartwood; is oily and smooth, with a faint odour, about the same weight as sandalwood, hard to very hard; slightly twisted-grained; texture fine and even. The growth rings are less distinct and are determined by narrow bands of dense fibrous tissue; 12 to 24 per inch. The very small pores, which are just visible with a hand lens, are mostly arranged in groups (Fig. 2), whilst the fine rays show distinct ripple marks on the tangential surfaces (Fig. 3).

D. G. H.

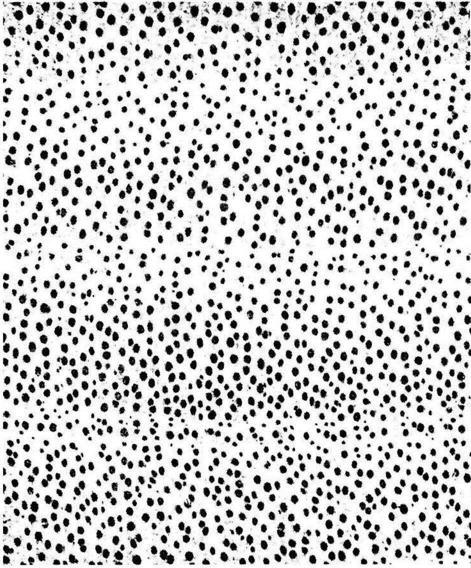

Fig. 1
Sandalwood

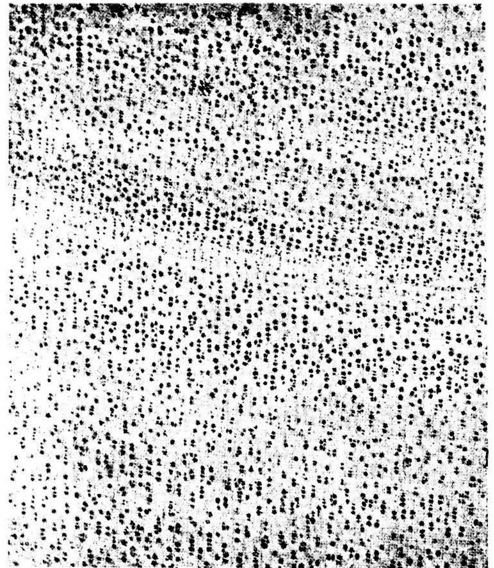

Fig. 2
Kalamet wood

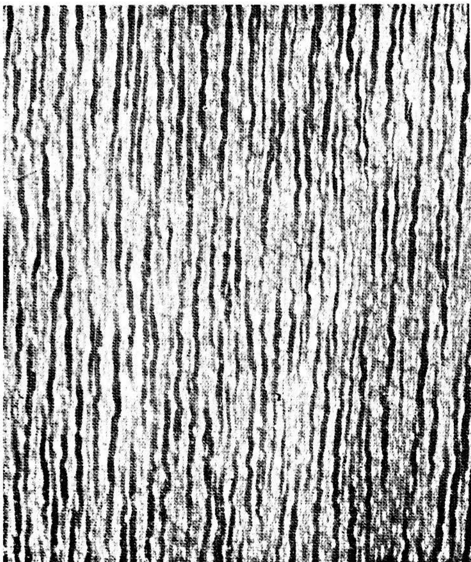

Fig. 3
Sandalwood

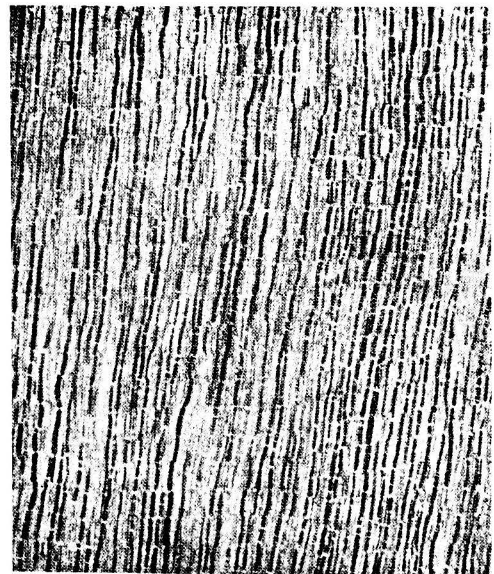

Fig. 4
Kalamet wood

Inorganic Analysis

Volumetric Determination of Iron using Basic Mercuric Bromate. G. F. Smith and H. H. Bliss. (*J. Amer. Chem. Soc.*, 1931, **53**, 4291–4297.)—Ferrous chloride in dilute hydrochloric acid solution is slowly oxidised by bromate at the ordinary temperature, whereas cuprous chloride is rapidly oxidised under similar conditions; the addition of a cupric salt serves as a catalyst in the oxidation of ferrous iron by bromate, since cupric chloride is reduced to cuprous chloride by ferrous chloride. There is a tendency for the cuprous chloride produced to become oxidised by the air before the titration is finished, but it has been found possible to overcome this difficulty by having arsenic acid present, an equivalent amount of which becomes reduced by the cuprous chloride, giving arsenious acid, which, while being unoxidised by the air, is rapidly oxidised by bromate in the cold solution. The following method was adopted for the determination of iron.—To the boiling solution of the ferric iron (containing 10 c.c. of concentrated hydrochloric acid in 25 to 50 c.c.), stannous chloride solution is added, drop by drop, until the yellow colour is discharged, and then one drop in excess. The solution is diluted to 80 c.c., and cooled to room temperature. Ten c.c. of mercuric chloride solution (10 per cent.) are added. Then 10 c.c. of catalyst solution (containing 4 grms. of copper sulphate crystals, 100 grms. of ammonium arsenate, and 500 c.c. of phosphoric acid diluted to 1000 c.c.), and a few drops of fuchsine indicator (strength not stated) are added, and the solution is titrated at room temperature with $N/10$ basic mercuric bromate solution until the indicator is decolourised. The formula of basic mercuric bromate is stated to be $HgOHBrO_3$, but the method of calculating the amount of iron from the amount of bromate solution used is not given; the analytical method does not appear to have been checked against independently known amounts of iron. Certain organic substances, *e.g.* tartaric acid, citric acid, acetic acid, may be present without interference, but formic acid must be absent. It is stated that potassium bromate cannot be substituted for the basic mercuric bromate, since it was found to give slightly low results. The preparation of basic mercuric bromate is not described in the paper (it is given in *J. Amer. Chem. Soc.*, 1924, **46**, 1577); the substance is stated to be now obtainable commercially.

S. G. C.

Separation of Manganese as Peroxide from other Metals. K. A. Jensen. (*Z. anal. Chem.*, 1931, **86**, 422–438.)—A critical study of the persulphate method gave results more or less at variance with those of Majdel (Analyst, 1930, **55**, 649). In accordance with the experience of other investigators, it was found practically impossible to avoid occlusion of a number of other metals, so that, whilst persulphate precipitation can be used as a step in the volumetric determination of manganese, it cannot pass muster as a precipitant quantitatively separating manganese from all the other common metals. Separation from silver, iron, and cobalt is not feasible. The alkalis are slightly adsorbed; bivalent metals are more or less freely occluded. Thallium, titanium, zirconium, thorium, and the acids of molybdenum, tungsten, and vanadium are co-precipitated. A satisfactory separation by a single precipitation, followed by thorough washing, is possible

in the case of the alkalis, beryllium, magnesium, aluminium, and chromium (the latter is oxidised to chromate). Double or treble precipitation (the precipitate being dissolved in sulphurous acid) achieves a quantitative separation from zinc and nickel. If the concentration of the sulphuric acid in the solution is higher than 0·6 *N*, the precipitated peroxide is so finely divided that a turbid filtrate results. The general conclusion is that the process has a certain importance for separations involving the above-named metals, but cannot be used as a general separation procedure. W. R. S.

Sensitive Test for Vanadium. F. Ephraim. (*Helv. Chim. Acta*, 1931, **14**, 1266–1269.)—The test, which is stated to have a sensitiveness of 1:400,000, is based on the reaction $V_2O_4 + Fe_2O_3 \rightleftharpoons V_2O_5 + 2FeO$, which takes place from right to left in an acid, but from left to right in an alkaline, medium. The ferrous salt formed is made to react in presence of ammonia with dimethylglyoxime, an intense cherry-red colour being produced. The reduction of vanadate to vanadyl salt is ensured by boiling with hydrochloric acid. One c.c. of solution and one of strong hydrochloric acid are boiled down rapidly to 0·4 c.c. After being cooled in water, the liquid is treated with one drop of fresh 0·1 per cent. ferric chloride, 2 drops of 1 per cent. dimethylglyoxime solution, and excess of strong ammonia: a more or less deep coloration is obtained according to the amount of vanadium present. It is soon bleached unless atmospheric oxidation is prevented by a layer of petroleum spirit. Reduction of the ferric salt by any other substance must be guarded against: no tartaric acid should be present, and the solution should be well cooled before addition of the alcoholic reagent. Chromates also are reduced by hydrochloric acid, though less readily than vanadates; the resulting chromic salt forms a violet ammine compound, though its colour is not strong enough to be taken for the coloration produced by the ferrous compound. W. R. S.

Volumetric Determination of Potassium. Austerweil and Lemay. (*Bull. Soc. Chim.*, 1931, **49**, 1541–1542.)—The following process, which occupies about 2½ hours, is advocated.—The test solution is rendered slightly alkaline, and any ammonia present is removed by boiling; it is then acidified with acetic acid (if the test solution contains cyanide or carbonate it must first be acidified with hydrochloric acid and boiled to remove these radicles). The potassium is precipitated as cobaltinitrite by the addition of an excess of sodium cobaltinitrite reagent (a mixture of 800 grms. of 25 per cent. aqueous cobalt nitrate solution, 1 kilo. of 40 per cent. sodium nitrite solution, with 200 grms. of glacial acetic acid, added in small portions at a time); about 40 c.c. of the reagent are required for 0·5 grm. of potassium. The liquid is diluted with one-third of its volume of ethyl alcohol (90 per cent.), heated on a water-bath for about half-an-hour, allowed to cool, and kept for about an hour and a half. The precipitate is filtered off on a sintered-glass crucible and washed with a little water. The crucible is transferred to a porcelain dish, and the precipitate dissolved by heating with 100 c.c. of "dilute" hydrochloric acid. The resulting solution is neutralised with sodium hydroxide, using litmus paper as indicator, and an excess of *N* sodium carbonate solution is added to precipitate the cobalt as carbonate. The liquid is diluted to

a known volume, and an aliquot part is filtered off, in which the excess of sodium carbonate is titrated with $N/5$ hydrochloric acid. One c.c. of N sodium carbonate solution = 0·039 grm. of potassium. No test results are cited, but the method is stated to give results accurate to 0·5 to 1·5 per cent. S. G. C.

Microchemical

Filter for Micro-gravimetric Analyses. P. L. Kirk and R. Craig. (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 345–347.)—The apparatus is suitable for the determination of phosphates, halides and sulphates. Instead of Pregl's method of transferring the precipitate being used, the precipitating vessel is made from a test tube attached to a tapered tube which is ground to fit the filter tube. The stopper of the precipitating tube consists of a hooked glass rod ground in to the tapered tube, which is removed after precipitation, to allow filtration. The filtering surface of the filter tube, which is about 1 cm. from the bottom of the ground-glass connection, consists of a platinum plate, made from foil, 0·005 inch (0·127 mm.) thick, containing small punched holes, 0·5 mm. or less in diameter. This plate is covered with a thin layer of pure washed asbestos. Glycerin is used as a lubricant for the ground-glass connections. Slight suction is used for the filtration. The filter tube is usually weighed alone, but when the precipitate adheres to the side of the precipitating vessel, both may be weighed together; the use of acetone, however, generally prevents the precipitate from sticking. Determinations, with an error of less than ±2 per cent., were made on varying quantities of the order of 1 mgrm. of chloride and sulphate. The barium sulphate precipitate was not ignited, but dried in Pregl's regenerating block. J. W. B.

Tests using Organic Reagents: Effect on the Sensitiveness of Increasing the Size of the Molecule. J. V. Tamchyna. (*Mikrochem.*, 1931, **9**, 229–241.)—Two examples are taken of tests for inorganic ions, using organic reagents, and a number of compounds of increasing molecular weight containing the reactive grouping have been tested. *Copper.*—The formation of yellow copper salts, which is characteristic of all xanthates, is due to the · · O.CS.SH · · grouping. Increasing the molecular weight of the reagent increases the sensitiveness of the test, owing to the decrease in solubility of the resulting compound, but the colour remains the same. The increase in sensitiveness is greatest between ethyl, butyl and amyl xanthate; cetyl and myricyl xanthate are very little more sensitive. The test is carried out on different strengths of copper sulphate, in total volumes of 1 c.c., when 0·1 c.c. of xanthate solution is added, and 5 c.c. when 0·5 c.c. of reagent is added; two drops (0·5 c.c.) of N hydrochloric acid are then added, and, if necessary, the mixture is heated to 70° C. The xanthate reagent is used in a 0·5 per cent. aqueous solution of the potassium salt. Cetyl and myricyl xanthate, since they are too insoluble in water, are used in saturated alcoholic solution, and 0·2 c.c. and 1 c.c. respectively, are added to the test solutions. The sensitiveness of the reaction is shown in the following table:

	Reagent.	Smallest amount of copper detectable in 1 c.c. γ	Limit of dilution.	Smallest amount of copper detectable in 5 c.c. γ	Limit of dilution.
1.	$SK{-}C(=S){-}O.C_2H_5$	1·20	1:850,000	5·0	1:1,000,000
2.	$SK{-}C(=S){-}O.CH_2.CH(CH_3)_2$	0·75	1:1,300,000	2·0	1:2,500,000
3.	$SK{-}C(=S){-}O.CH_2.CH_2.CH(CH_3)_2$	0·75	1:1,300,000	1·5	1:3,300,000
4.	$SK{-}C(=S){-}O.C_{16}H_{33}$	0·50	1:2,000,000	1·0	1:5,000,000
5.	$SK{-}C(=S){-}O.C_{30}H_{61}$	0·50	1:2,000,000	1·0	1:5,000,000
6.	Viscose	2·5	1:400,000		

Molybdates.—These also react with potassium xanthate, forming a yellow-red precipitate which rapidly turns violet. The results in the table resemble those obtained with copper. The test was carried out in the same way.

	Reagent.	Smallest amount of molybdate detectable in 1 c.c. γ	Limit of dilution.
1.	$SK{-}C(=S){-}O.C_2H_5$	2·0	1:500,000
2.	$SK{-}C(=S){-}O.CH_2.CH(CH_3)_2$	0·65–0·74	1:1,500,000
3.	$SK{-}C(=S){-}O.CH_2.CH_2.CH(CH_3)_2$	0·5	1:2,000,000
4.	$SK{-}C(=S){-}O.C_{16}H_{33}$	0·5	1:2,000,000
5.	$SK{-}C(=S){-}O.C_{30}H_{61}$	0·5	1:2,000,000

The tests may also be carried out on filter paper, using a drop of test liquid, when the smallest amount recognisable is less than 0·1γ, but the limit of dilution is not so great, 1:500,000.

Silver.—The tests for silver, using rhodanine derivatives, also show that the sensitiveness increases with increase of molecular weight. When a benzene ring is present in the molecule, the colour intensity is greater, and this considerably increases the sensitiveness of the test. The reagents are all used in 0·05 per cent. alcoholic solution. The test solutions are made slightly acid with nitric acid. The colour change is visible in 3 to 5 minutes.

	Reagent.	Smallest amount of silver detectable in 1 c.c. γ	Limit of dilution.
1.	HN — CO SC CH_2 \ S /	13–14	1:70,000
2.	HN — CO SC C=CH.CH_3 \ S /	10	1:100,000
3.	HN — CO SC C=C<CH_3, CH_3 \ S /	8·4–8·7	1:115,000–1:120,000
4.	HN — CO SC C=C<CH_3, $CH_2.CH_3$ \ S /	8·4	1:120,000
Phenyl derivatives. 1.	HN — CO SC C=CH.C_6H_5 \ S /	5 (visible ppt.) 0·4 (colour change)	1:200,000 1:2,500,000
2.	HN — CO SC C=CH.$C_6H_4.CH_3$ \ S /	5 (visible ppt.) 0·4 (colour change)	1:200,000 1:2,500,000
3.	HN — CO SC C=CH.$C_6H_3O_2CH_2$ \ S /	5 (visible ppt.) 0·5 (colour change)	1:200,000 1:2,000,000

J. W. B.

Micro-Determination of Sodium in Biological Materials. R. A. McCance and H. L. Shipp. (*Biochem. J.*, 1931, **25**, 1845–1848.)—McCance and Shipp (*Biochem. J.*, 1931, **25**, 449) described a colorimetric method for the micro-determination of sodium (0·02–0·8 mgrm.). The technique is now given for its application:—(*a*) without the necessity for incineration, to blood-serum, milk, cerebro-spinal fluid and urine, and (*b*) to solid tissues, with incineration. *Whole Blood and Serum.*—Trichloroacetic acid is used to precipitate the proteins. To about 8 c.c. of water in a 25 c.c. flask 0·5 c.c. of serum (or 1 c.c. of whole blood) is added, and then with shaking 1 c.c. of 30 per cent. trichloroacetic acid (or 3 c.c. in the case of

whole blood). This is left for 5 minutes, made up to the mark, mixed, and filtered through an ash-free paper; 1 c.c. of the filtrate is taken for each sodium determination, which is carried out as previously described. In whole blood determinations ammonium oxalate is used in place of lithium oxalate as an anti-coagulant. *Cerebrospinal fluid.*—The technique is exactly the same as for blood-serum. *Urine.*—In urine there is usually enough sodium available to enable macro-methods to be used, but for investigations on small experimental animals or even insects a micro-method is desirable. An accurate 1 in 25 or 50 dilution of the urine is prepared, and 1–2 c.c. of this diluted urine are taken and treated as described previously. *Milk.*—Bromine is used as the protein precipitant. Five c.c. of milk are placed in a 50 c.c.-flask, and diluted to about 15 or 20 c.c. with distilled water; 10 c.c. of saturated bromine water (for human milk) or 15 c.c. (for cow's milk) are then added, and, after shaking, the volume is made up to 50 c.c., and the suspension is filtered through an ash-free paper. For each determination 1 to 1·5 c.c. of the filtrate (which should be yellow) is taken, the phosphates are removed with zinc acetate in 50 per cent. alcohol, and the sodium is determined, as usual, by precipitation with uranyl zinc acetate. *Solid tissues.*—The method is applied to hydrochloric acid extracts of incinerated material. An inexpensive incineration apparatus, to take the place of an electric muffle furnace with graduated resistance, is described. Tables show the results obtained by the new method for body fluids compared with an incineration method, and the recoveries of known amounts of sodium added to various body fluids. P. H. P.

Physical Methods, Apparatus, etc.

New Micro Melting-Point Apparatus. L. Kofler and H. Hilbck. (*Mikrochem.*, 1931, 9, 38–44.)—An electric heating plate is described for observing melting points or sublimation under the microscope. It is similar to Klein's apparatus (*Mikrochem. Pregl-Festschrift*, 1929, 192), except that the temperature is measured by means of a thermo-couple, instead of a thermometer imbedded in the copper heating block. The authors found errors of 4° to 8° C. when using Klein's apparatus at high temperatures, but, with a heating plate with the temperature measured (using a copper-Constantin element) the maximum error was reduced to ±1° C. up to 200° C., and to ±2° C. between 200° and 300° C., when for the final 10° before the melting point the temperature was not allowed to rise more than 1° to 2° per minute. The apparatus is suitable for magnifications up to 135 diameters. J. W. B.

Simple Fluorescence Microscopy and Fluorescence Photomicrography. P. Metzner. (*Mikrochem.*, 1931, 9, 72–91.)—A parabolic mirror (Busch) is described, made of a metal which strongly reflects ultra-violet light, for attachment to the microscope in observing fluorescence phenomena in incident light. The mirror focuses the ultra-violet light on to the object to be observed, and renders sufficient the illumination obtained from an ordinary quartz or mercury lamp. The illumination can be still further increased by interposing a round glass flask filled with distilled water, as a focusing lens, between

the lamp and the black ultra-violet light-filter, and so adjusted that the image of the lamp falls on the mirror. This is better than a large lens, which would absorb some ultra-violet light. When an arc lamp is used, nickel is preferable to carbon, as it emits more ultra-violet light. The condenser lens of the arc lamp, which may be of ordinary glass (though Uviol glass is better) is adjusted to give almost parallel light which falls horizontally on the parabolic mirror. An ultra-violet light-filter is placed between the lamp and the microscope, and, to absorb red rays the beam is passed through a half-saturated solution of copper sulphate in a container made of two thin-walled glass plates held together by a thick rubber ring, in which are two holes for filling. The illumination by means of the parabolic mirror is suitable for use with low-power objectives (up to Leitz 5). For photographic purposes it is necessary to use a "Euphos" cover-glass (Zeiss), or an ultra-violet light-filter to cut out any ultra-violet light that may be reflected. A number of photographs were taken of plant material in a non-fluorescing medium (water or glycerin). The time of exposure varied from 20 to 60 minutes.

J. W. B.

Fluorescence Microscopy with Strong Illumination. M. Haitinger. (*Mikrochem.*, 1931, 9, 430–440.)—Faintly fluorescing substances, such as the chlorophyll in algae, are not sufficiently illuminated by mercury lamps or carbon arc lamps for microscopy. Brighter illumination is given by an arc lamp with iron as the electrode metal. Iron is the most suitable element, as it emits light a large percentage of which has wave-lengths between 3000 and 4000 Å.U. To maintain evenness of illumination and to prevent poisoning of the electrodes by formation of iron oxide, the electrodes are as short as possible, and imbedded in coolers of ribbed brass; they are also bored and filled with brass. With a direct current of 5 ampères the arc glows with sufficient regularity for hours. The light from the arc passes through a convergent lens of quartz or glass non-absorbent of ultra-violet light, then through a dark glass ultra-violet light-filter and a solution of copper sulphate, to absorb red rays, before being directed on to the mirror of the microscope. The loss of ultra-violet light on a silvered glass mirror, when the glass does not absorb ultra-violet light, is negligible. However, iron plated with chromium may also be used as a mirror. The light passes through a dark ground condenser of quartz, or glass which does not absorb ultra-violet light, on to the object. To prevent any ultra-violet light coming through to the eyes or photographic plate a stopping filter must be used; this cuts off the light between 3000 and 4000 Å.U. As the illumination is very bright, short exposures of a few minutes are sufficient for photographing the fluorescence. The apparatus is suitable for work at any magnification; for high powers the microscope is used horizontally and the mirror dispensed with, to avoid the slight loss of light. The dark-glass filter can be rapidly replaced by an opal glass filter for comparison with the appearance of the object in ordinary light. When non-transparent objects are viewed, incident light must be used; this is achieved by means of a periscope of two mirrors.

J. W. B.

Reviews

THE VITAMINS. By ETHEL BROWNING, M.D. (Liverpool). Pp. 575+xxxii. London: Baillière, Tindall & Cox. 1931. Price 42s.

This is much the largest book yet published about vitamins in English, or, indeed, as far as I know, in any language. The amount of labour that must have gone to its compilation is so enormous that the voice of criticism is almost drowned by the cheer of admiration. It contains, besides the text and a bibliography of at least 3000 references, 45 pages of tables showing the Vitamin Content of Foodstuffs, a number of diagrams and illustrations, 7 plates, and indexes of authors and subjects.

In Part II there is a discussion of vitamins in general; subsequent parts treat in detail of each known vitamin separately. The arrangement of the sub-sections under the heads of the individual vitamins is thorough and systematic. The author has deliberately emphasised the clinical aspect of the subject, and in so doing, has assembled much scattered information not previously obtainable without an exacting amount of search in the literature.

The body of the book consists mainly of a summary of published papers; it contains nothing in the way of commentary upon them. It is clear, from internal evidence, that the author has certainly read the "conclusions" of all these papers, not merely abstracts of them, and in many cases the papers themselves. The number of papers summarised appears to be of the same huge order as the number of references in the bibliography.

At the end of the book, after an Addendum of 10 pages, containing "information brought to the notice of the author too late to be incorporated in the general body of the text," is a section entitled "Author's Summary and Conclusions," occupying 22 pages, and constituting the only critical part of the book. Even here, however, it is the summary rather than the conclusions that receive emphasis, so that the book must be regarded almost solely as a book of reference.

Its nature is, therefore, such as to justify a demand for scrupulous accuracy in the record of the work done in vitamin research during the past twenty years. It is impossible fully to establish whether this demand is met, since it would take even longer to check all the statements made in the book than it must have taken to write it. One can at most indulge in some "random sampling," only selecting in so far as to choose the summaries of work with which one is best acquainted.

From such a test the book does not emerge unscathed. The first sentence at the top of p. 13 is quite incorrect (as is clear from statements later in the book): the "P.P." factor is not necessary for the normal growth of pigeons. On p. 133 it is stated that vitamin *D* forms an insoluble digitonide, and is destroyed by treatment with bromide. The second statement is probably due to a misprint; the first is quite untrue. Instances could also be given of chemical formulae and equations that are wrong, misleading or meaningless, and of the consistent mis-spelling of authors' names.

In general, the author is least useful when she is summarising the more definitely chemical aspects of the subject. In view of the existence of Sherman and Smith's excellent monograph (reviewed by K. H. Coward in the ANALYST, 1931,

56, 491), it would probably have been better to have rigorously restricted the treatment of those aspects, and to have laid more emphasis, and applied actual criticism to, the clinical aspects with which the author is so obviously more familiar. However, that would, in practice, have meant writing a different book from the one she has actually written and presumably intended to write, and, though such a book is still needed, a reviewer is mainly concerned with noting how far an author has carried out his avowed object, and the comment must be regarded rather as an *obiter dictum* than as fair criticism. It cannot for a moment be denied that this almost monumental volume has great value as a repository of present-day knowledge about vitamins.

Unfortunately, the utility of the book has been unforgiveably limited by the publisher's parsimony. The volume measures $11 \times 8\frac{1}{2} \times 2$ inches, and weighs a shade under 4 lbs. It is a book that will certainly be used mainly as a reference book, and will therefore be handled for short periods, but repeatedly. Its price means that few will buy it who do not definitely need it—that is the almost inevitable fate of *biblia abiblia*, especially if they have over 600 pages. Had its price been a few shillings more, its circulation would probably have been unaffected. So that even considerations of economy do not really afford the least justification for the fact that it is published—*in paper covers!* A. L. BACHARACH.

COLLOID ASPECTS OF FOOD CHEMISTRY AND TECHNOLOGY. By WILLIAM CLAYTON, D.Sc., F.I.C. Pp. vii+571; with 64 illustrations. London: J. & A. Churchill. 1932. Price 36s.

As a sign of the fundamental changes which have occurred in the chemical industrial outlook during the last twenty or thirty years, one has only to compare the scope and character of an industrial text-book of that date with those of a work such as the one which has just come from Dr. Clayton's pen. In the earlier days the treatment of a subject was, in the main, descriptive, stress being usually laid upon procedure which was inevitably empirical, and, what was even more significant, without any apparent realisation of the essential superficiality and lack of correlation inherent in such a treatment. A compilation of this older type recorded current practice, but was, on the whole, incapable of suggesting new lines of investigation which it would be worth while to pursue, for the very good reason that investigation was considered as something so remote from practice that it was unlikely to possess any direct, *i.e.* economic, value.

That the present attitude is very different is readily demonstrated by an examination of a work such as that before us. It is written for, and intended to be read with profit by, those directly concerned with industrial processes. It is, therefore, significant that the author has obviously no hesitation in giving considerable space to those principles of a purely scientific character which he clearly regards as the only means available wherewith to attack the specific problems which food technology presents.

As is to be expected in a work planned and developed along these lines, the whole subject is seen to bristle with problems inviting further research. The presentation is attractive and can scarcely fail to arouse in others something at least of the enthusiasm which the author himself so evidently possesses.

The precise object which the author has had in view is best described in his own words:—"It is not a treatise on food technology, but rather an introductory guide to those aspects and problems of a colloid nature which may be unfamiliar to the food chemist who has not specialised in colloid chemistry and physics."

A general idea of the scope of the work will be gathered to some extent from the chapter titles, which are as follows:—Agar-agar and gums (with particular reference to swelling under different conditions and the electro-viscous behaviour as worked out in Kruyt's laboratory); the colloidal behaviour of proteins (a vast subject excellently epitomised); a special chapter on gelatin (including its use as an emulsifying agent, its behaviour in respect of swelling, capillary activity, viscosity, the problem of turbidity of gelatin solutions, the setting of gelatin and the structure of the gel); the colloid chemistry of the starches, flour and its protein constituents (the strength of flour, the colloidal behaviour of dough and the staling of bread); the properties of emulsions and the theories of emulsification (as applied to butter, margarine, salad dressings, medicinal emulsions and the rôle of emulsions in bread-making); milk and milk products (including the problem of the stability of such systems, the principles underlying churning, homogenisation, coagulation by rennin, cheese and ice-cream); colloid aspects of nutritional chemistry; colloid problems in sugar technology (including molasses, caramel, honey, with the decolorising and other adsorptive processes operative in such systems); fruits, jams, jellies and marmalades (including the fundamental pectin-sugar-acid equilibrium); colloid phenomena in brewing (including, among other topics, the change in the electric charge exhibited by yeast, the surface tension of beer as a function of *p*H and the problem of frothing, beer haze and the Ramsden phenomenon, and the fining of wine); the freezing and thawing of colloid systems (with special reference to the preservation of foodstuffs, the account being based, in the main, upon the remarkable series of researches initiated by Sir W. B. Hardy on behalf of the Food Investigation Board at Cambridge); and, finally, the treatment of water and factory effluents.

In addition, there is included an extensive bibliography, occupying approximately 100 pages, divided into sections for convenience in reference. This, of itself, is evidence of the labour and enthusiasm which the author has brought to bear in order to make the work as complete as possible.

It is obvious that no single reviewer is competent to assess the value of a work which covers such a wide field. The best that one can do is to examine in particular those sections with which one has some degree of familiarity, and to form a judgment on that basis. Examining it in this way, the present reviewer has no hesitation in strongly recommending the book as an eminently successful effort to co-ordinate and correlate apparently very diverse procedures in systems which, at first sight, might appear to have little in common.

The author has had a wide experience in the field of colloids, more particularly as applied to the food industries. It is not surprising, therefore, that the present work emphasises the vital part which scientific principles—in this case the principles of colloid physics and chemistry—play in the development of these industries. For this reason Dr. Clayton's book is indispensable to all engaged, not only in the industries referred to, but in all other branches of chemical industry in which colloids play a part.

W. C. M. Lewis.

FORENSIC CHEMISTRY AND SCIENTIFIC CRIMINAL INVESTIGATION. By A. LUCAS, O.B.E., F.I.C. Pp. 324. London: Edward Arnold & Co. 1931. Price 18s. net.

The term "medico-legal" is still too often loosely used to describe work which is essentially of a chemical nature, and the author of this book rightly lays stress upon the point that there is no justification for a statement such as the following from a work on circumstantial evidence: "One of the most valuable functions of the medical profession is the detection of poison, blood and other matters by chemical examination." The true scope of forensic medicine is distinct from that of forensic chemistry, which, however, now embraces such subjects as the examination of counterfeit coins, documents, stains, etc., which are only partly chemical, and involve the use of the microscope and of physical methods.

Ten years have passed since this book was first published and was reviewed in THE ANALYST (1921, **46**, 529), and in the interval so many advances have been made in nearly every branch of scientific criminal investigation that the author has done well to emphasise this aspect of his work in a sub-title. The excellent plan of arranging the various sections in alphabetical order has been retained; it adds much to the value of the book as a work of reference. Some of the sections have been condensed and others re-arranged or amalgamated; the section on "Stains and Marks," for instance, has been incorporated with "Dust and Dirt," and "Hashish" is now included among the poisons. But even after these changes the size of the book has been increased by fifty-six pages. The section on "Blood-stains" has been entirely re-written, and now includes a concise description of the determination and significance of blood groups. There is also much new matter in the sections on "Explosions and Explosives" and on "Firearms, Cartridges and Projectiles," which now have a scientific literature of their own.

The section on "Poisons" has been completely revised, and includes many additional poisons, such as carbon monoxide, chloral and chloroform, as well as a method for the isolation of veronal from viscera.

Among the important additions to the section on "Documents" are methods for the examination of burnt documents and tests for sizing materials on paper, and the use of fluorescence tests is discussed under this heading, as well as under "Microscopy, Photography and Ultra-Violet Rays," and under "Robbery from Letters and Parcels."

As the Introduction is essentially a valuable summary of the whole practice of forensic chemistry, it will not be out of place to refer to it last. It gives concisely the rules to be observed when receiving exhibits, and deals with their examination, with the writing of reports, and with the presentation of evidence in Court. The author's caution that it is essential to define the exact sense of such terms as "a small amount" or "a trace" will be endorsed by everyone who has tried to get concise definitions of those quantities from a number of chemists. A word of warning, perhaps, is necessary in connection with the author's advice (p. 16) to put a distinguishing mark upon a document. Unfortunately, this practice does not always commend itself to a judge, for as recently as last November Mr. Justice Swift, in the case of *Riddle and Holder* v. *The Midland Bank, Ltd.*, emphatically laid down the dictum that in no circumstances should any mark whatsoever be made upon a document which was to be produced in evidence.

Space does not allow of more than a brief outline of the contents of this work,

but sufficient has been said to show how wide is its scope. Mr. Lucas has had exceptional opportunities of applying scientific methods to criminal investigation, and has made full use of them, with the result that his book has a unique position as a work of reference. Every chemist in a consulting practice is at times confronted with out-of-the-way problems involving the identification of materials, and here he will usually find the solution, together with copious references to previous work on the subject. This edition fully maintains the reputation which the author won with its predecessor. EDITOR.

THE MICROSCOPICAL EXAMINATION OF CATTLE FOODS. By S. T. PARKINSON, B.Sc., and W. L. FIELDING, B.Sc., Agric., Dip. Agric. Pp. viii+97. Illustrated with 15 plates, comprising 125 original photographs. Headley Brothers, The Invicta Press, Ashford, Kent, and 18, Devonshire Street, E.C.2. 1930. Price 6s. 6d. net.

The present volume gives a detailed description and pictorial representation of the microscopical appearance of cattle foods, in a form which can be highly recommended to students and also to chemists engaged in the analysis of these articles. The introductory part describes in a practical way the preliminary physical and chemical tests which should be applied in the macro-examination of a cattle food, and, also, the use of the microscope, sources of illumination, and methods of sketching the fragments and making permanent preparations.

The principal food plants are divided into three groups: oil-containing plants, cereals and leguminous plants. Each plant is described separately, and the authors have given an analytical value to the treatment of each group by cross-references in the descriptions to similarities and differences between the various plants, but especially by means of folded pull-out sheets which describe, in condensed tabular form, the macroscopic character and the microscopic appearance of related layers of tissues in each plant of the group.

A microscopist with his finger continually on the fine adjustment can see the forms of thick tissues which are very difficult to reproduce in a photograph, and it is debatable whether sketches or photographs are more suitable for portraying such tissues. The authors have been generally successful in obtaining clear photographs of the tissues, though an exception must be noted in the case of the rice husk picture, which fails to show the wavy character of the cells. A consistent use of one letter to denote the same layer in the different pictures assists comparison.

Miscellaneous constituents of cattle foods, such as sphagnum, cacao shells and weed seeds, are described in a final part, in which the pictures are confined to slightly magnified photographs of the unbroken small seeds, to assist in their macroscopic detection.

Two omissions have been noted. There is no reference to fish or meat tissues, which are frequent constituents of mixed foods, and the meaning of the term μ, used as a dimension in measuring microscopic objects, is not explained.

The volume closes with a bibliography of related works and a very good index. It is bound in a useful form which allows the pages to lie flat on a work-bench, and the price is reasonable. It will be a useful book of reference and textbook for agricultural chemists and students. A. MORE.