THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 3rd, Mr. John Evans, President, being in the chair.

Certificates were read in favour of:—William Godden, B.Sc., F.I.C., and Frank Morton, B.Sc., A.I.C.

The following were elected members of the Society:—Frank Bell, Ph.D., D.Sc., F.I.C., James Talmage Dobbins, A.M., Ph.D., Daniel Joseph O'Sullivan, M.Sc., F.I.C.

The following papers were read and discussed:—"Commercial Ground Almonds and their Adulteration," by G. N. Grinling, F.I.C.; "The Detection of Japanese Mint Oil in Peppermint Oils," by D. C. Garratt, B.Sc., Ph.D., F.I.C.; "Measurement of the Small Volumes of Nitrogen obtained by the Micro-Dumas Method," by H. C. Gull, M.Sc.; and "The Application of Analysis to the Study of Liesegang Rings," by E. B. Hughes, M.Sc., F.I.C.

NORTH OF ENGLAND SECTION

ON the invitation of Mr. Arnold R. Tankard, F.I.C., a meeting of the Section was held at Hull on April 6th, 1935. There was an attendance of thirty-seven; the Chairman (Professor W. H. Roberts) presided.

After a short address, given by Mr. Tankard, the members inspected the new analytical and bacteriological laboratories of the City of Hull.

Deaths

WITH deep regret we record the following deaths:—

Leonard Archbutt (Past-President),
Charles Frederick Cross,
Arthur John Starey.

Obituary notices will be published later.

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

XXVIII. The Separation of the Rare Earths from the Earth Acids

By W. R. SCHOELLER, Ph.D., F.I.C., and E. F. WATERHOUSE

(Work done under the Society's Analytical Investigation Scheme)

From the point of view of their rare-earth (*i.e.* yttria- and ceria-earth) content, earth-acid minerals may be subdivided into two groups: (1) Those containing rare earths as essential or major constituents; and (2) those in which the rare earths occur in subordinate down to minute quantities. The analysis of minerals of the first group is discussed in Part I of this section; the determination of the small amounts of rare earths in minerals of the second group forms the subject of Part II.

The pure preparations of ceria, lanthana, neodymia, and thoria used in this research were kindly placed at our disposal by Messrs. Thorium, Limited, through their works manager, Mr. H. F. V. Little, who was also good enough to criticise the manuscript of this paper.

PART I. Minerals Rich in Rare Earths

The better-known of these exceedingly complex minerals are fergusonite, samarskite, yttrotantalite, euxenite, and aeschynite. It may be noted that the ceria earths preponderate over the yttria earths in aeschynite, the reverse being the case in the other four species.

The analysis of minerals of this class has been greatly facilitated by the labours of J. Lawrence Smith, to whom we owe the process based on decomposition of the mineral by hydrofluoric acid.[1] The earth acids (and titania, zirconia, and tungstic acid) thus go into solution, whilst the rare earths and thoria are converted into insoluble fluorides. Hillebrand and Lundell[2] describe the method and comment upon it in the following terms: "When applicable it should always be used, for it affords very quickly and easily an almost perfect separation of the insoluble rare-earth and alkaline-earth fluorides from the soluble fluorides of the earth-acid and other metals. The method introduces no alkali salts, and has the further advantage, shared by no other, not only of showing whether quadrivalent uranium is present, but also of separating it from sexivalent uranium if both are present."

Smith's process has been studied by Hillebrand[3] and by Wells.[4] The latter's paper is particularly valuable, as it shows the quantitative distribution of the mineral constituents between the fluoride solution and the insoluble fluoride fraction in a samarskite analysis, Wells observing that the method "is not as simple or clean-cut in its separations as the original description might lead one to suppose." However, the summation of his results shows that the earth acids and titania (as well as the small amounts of tin, tungsten, and zirconium present) are found wholly in the fluoride solution, whilst the insoluble fraction contains the

whole of the rare earths and thoria. Uranium, being present in the uranous, as well as the uranic, condition, figures in both fractions. The eight remaining constituents, shown by Wells to distribute themselves between the two fractions, are all common elements. We may sum up his experimental evidence by saying that a quantitative separation of the rare earths and thoria from the earth acids, titanium, tungsten, etc., is achieved, but that a number of common elements will be found in the solution as well as in the precipitate. Their distribution between the two fractions is a minor disadvantage of this valuable process, as the two fractions, after the recovery of the rarer elements contained therein, may be combined for the determination of the common metals.

In Smith's process the insoluble rare-earth fluorides are filtered off and converted into sulphates for analysis by the usual methods. The fluoride filtrate also is evaporated with sulphuric acid until the whole of the hydrofluoric acid is expelled; the acid is diluted with water, and the liquid boiled for the hydrolytic precipitation of the earth acids. Instead of using that time-honoured procedure, the disadvantages of which we have discussed in Section XII,[5] we dissolve the acid residue in tartaric acid (with or without previous conversion into a bisulphate melt), according to the general plan laid down in Section I.[6] This course is recommended also by Hillebrand and Lundell.[2] We are now endeavouring to effect the quantitative recovery of the small amounts of tungsten, generally present in the minerals under discussion, from the tartrate solution containing substantial quantities of earth acids with titania and zirconia. The investigation will, we hope, form the subject of a separate Section.

Our experimental work, described in Part II below, has convinced us that the direct application of Schoeller and Powell's scheme of bisulphate fusion and tartaric-acid leaching to minerals containing the earth acids and rare earths as chief constituents, would be inconvenient and even undesirable. Inconvenient, because the solution of the bisulphate melt in tartaric acid would be complicated by the formation of sparingly soluble, double rare-earth sulphates; and undesirable, because the recovery of large amounts of rare earths from tartrate solutions containing earth acid, titania, etc., is less accurate, at any rate, than the fluoride method. We are satisfied that J. L. Smith's process, whilst doubtless requiring further study, is by far the best procedure for the analysis of the minerals here discussed.

PART II. Minerals Poor in Rare Earths

The principal object of this investigation was to study the analytical problem of the recovery of small quantities of rare earths from tartrate solutions containing earth acids, since fusion with bisulphate and lixiviation with tartaric acid form the starting-point of our scheme outlined in Section I.[6] Before discussing that work we will briefly describe our investigation of a procedure suggested by Pied[7] for the isolation of the rare earths and thoria from earth-acid minerals.

A. Pied's Proposed Procedure.—Pied's paper deals with the precipitation of the earth acids by cupferron[8] from oxalo-tartaric solution after the removal of iron as sulphide. The paper concludes with a seven-line paragraph containing the following passage in literal translation: "I have ascertained that the oxalic solution

[of the earth acids] can be obtained by direct treatment of the fused mass obtained from the calcined oxides and many minerals by an attack with pyrosulphate. The rare earths and thorium do not hinder the dissolution; they form a crystalline precipitate, the size of which allows of their evaluation (*dont l'importance permet d'évaluer leur teneur*) in the mineral."

We are not sure whether the quotation from the French text is to be interpreted in a quantitative sense, especially as the paper contains no numerical data. However, we considered the proposed procedure sufficiently interesting for a quantitative investigation. A number of tests were conducted with lanthana, ceria, neodymia, yttria, and thoria, with and without earth acids.

The oxides were fused with potassium bisulphate (3 g.), and the fused mass was extracted with 100 ml. of hot oxalic acid solution (2 to 6 per cent.); the liquid was allowed to stand in the cold, either overnight or some days. The precipitate was collected, washed with weak oxalic acid solution, ignited, and weighed. Only the lanthanum oxalate was markedly crystalline; the others were more or less amorphous, and accordingly did not filter well. The test separations of rare earths from the earth acids gave indifferent results. We need not reproduce more than four, in which 2 per cent. oxalic acid solution was used for extracting the bisulphate melt:

Exp.	Taken g.	Added g.	Ignited oxalate ppt. g.
1	La_2O_3 0·0132	Ta_2O_5 0·1542	0·0416, containing Ta_2O_5
2	,, 0·0125	Nb_2O_5 0·1534	0·0113. Error — 0·0012
3	CeO_2 0·0170	Ta_2O_5 0·1550	0·0417, containing Ta_2O_5
4	,, 0·0189	Nb_2O_5 0·1512	0·0184. Error — 0·0005

The tests disclose a marked difference between tantalic and niobic oxides. Whilst the latter was readily soluble in the reagents used, the former contaminated the oxalate residue to such an extent that the ignited precipitate contained more tantalic oxide than rare earth. This is explained by the fact that oxalic acid is a poor solvent for tantalic oxide: Britton and Robinson[9] state that 0·3 g. required a solution containing 9 g. of crystallised oxalic acid. The use of larger volumes of solvent would be attended with an increased negative error, caused by the slight but appreciable solubility of the rare-earth oxalates. We tried application of 6 per cent. oxalic acid, but experienced trouble in the deposition overnight of coarse crystals of potassium quadroxalate. We tentatively applied leaching of the bisulphate melt with ammonium oxalate solution which, though a more efficient solvent for tantalic-oxide melts, has the disadvantage of dissolving perceptible quantities of the oxalates of the yttrium group; and, whilst it dissolves thorium oxalate, it does not bring about a complete separation of thoria from the rare earths. Of three tests with tantalum and cerium, two gave oxalate precipitates contaminated with tantalum; one gave a correct result. Two tests with tantalum and lanthanum proved a failure: the precipitate slimed badly in one test, and in the other the lanthana recovery showed a large negative error.

We came to the conclusion that the method proposed by Pied is not suitable for quantitative separations of amounts exceeding a few centigrams. In Exps. 14 to 20, described below, the procedure worked satisfactorily with the small quantities involved.

Reactions of the Rare Earths in Tartrate Solution

These will be considered under three heads: (B) Precipitation of the Oxalates. (C) Action of Tannin. (D) Behaviour in Tartaric Hydrolysis.

B. Precipitation of the Oxalates.—This work was undertaken with a view to recovering subordinate amounts of rare earths, by means of oxalic acid, from the tartrate solution of a bisulphate melt containing earth acid.

The mixed oxides (0·15 g. of pentoxide and 0·015 g. of rare earth) were fused with bisulphate (3 g.), the melt was dissolved in 50 ml. of hot tartaric acid solution (6 to 8 per cent.), and the liquid (100 ml.) was treated with 10 ml. of saturated oxalic acid solution. After standing overnight, or for some days, the precipitate was collected, washed with dilute oxalic acid solution, and ignited to oxide.

It was found that, when much tantalum is present, the addition of oxalic acid to the tartrate solution causes gradual flocculation of tantalic acid. Digestion of the washed precipitate with fresh oxalic acid removes the tantalic acid, leaving the rare-earth oxalate. Such a procedure is again open to the objection that it may increase the slight solubility loss of rare earth; hence we do not consider it suitable for recovering small quantities of rare earths from tartrate solutions containing much earth acid. On the other hand, we have found it useful for quantities not exceeding a few cg., and have applied it in our separation method described below (under D, Exps. 21 to 28).

C. Action of Tannin.—The improvements achieved in the analytical chemistry of the earth acids and a number of other earths by the agency of tannin[10] induced us to investigate the possibilities of this reagent in the analysis of the rare earths; so far as we know, the subject had never before been studied.

We ascertained that tannin complexes of the rare earths are precipitated from their solutions on addition of tannin and an excess of ammonia. The precipitation takes place in tartrate solutions also. The precipitates are colourless, excess of tannin causing a pale-brown discoloration, as in the case of alumina; the cerium precipitate, however, darkens considerably on exposure to the air; it often turns almost black on the filter. Unlike the aluminium precipitate, the rare-earth complexes are readily soluble upon acidification with acetic acid of the liquid in which they are suspended; in this respect they behave like the precipitates of beryllium and manganese.[11]

For the quantitative investigation of the reaction we prepared solutions containing known amounts of cerium and of yttrium. Measured portions were diluted to 200 ml., boiled, and treated with the following reagents:—25 ml. of saturated ammonium chloride solution, 5 g. of sodium acetate, 0·5 g. of tannin in freshly-prepared solution, and ammonia (1 : 3) until its smell became pronounced. In the tartrate tests, tartaric acid (4 g.) was added before the ammonia. The precipitates were allowed to settle on the water-bath, collected, well washed with ammonium nitrate solution, ignited strongly, and weighed:

Exp.	Taken	Solution	Found	Error
	g.		g.	
5	CeO_2 0·0500	Acetate	0·0500	0·0000
6	,, 0·0500	Tartrate	0·0496	−0·0004
7	Y_2O_3 0·0508	Acetate	0·0522	+0·0014
8	,, 0·0508	Tartrate	0·0508	0·0000

Having demonstrated the quantitative recovery of the two earths from ammoniacal tartrate solution, as well as the ready solubility of their tannin complexes in dilute acetic acid, we proceeded to investigate the separation of small quantities of rare earths from the earth acids. The latter, it will be recalled, are quantitatively precipitated from feebly-acid tartrate solutions containing acetate.[8]

We conducted 9 experiments on mixtures of pentoxide and ceria. Tantalic oxide was taken in 5, niobic in 4, tests. It was found that partial co-precipitation of ceria (shown by the excessive weight and the yellow to buff colour of the ignited tannin precipitate, *TP*) took place under the conditions given in Section XVII[8] for the complete precipitation of the earth acids (Exp. 9, below). In a tantalum solution containing 5 ml. of acetic acid in 100 ml. total bulk, tannin produced no precipitate; subsequent neutralisation with ammonia until the pure yellow colour of the tantalum precipitate showed signs of bleaching (co-precipitation of traces of iron at the neutral point) gave a seemingly good separation (Exp. 10). These conditions and results could not be reproduced with niobium. In Exps. 11 and 12, the earth acid was precipitated from the tartrate solution half-saturated with ammonium chloride after neutralisation of the tartaric acid with ammonia, the resultant acidity of the solution being that of the pyrosulphate after fusion.

Exp.	Taken		Tannin added	Saturated NH_4Cl sol.	*TP*
	M_2O_5 g.	CeO_2 g.	g.	in 250 ml.	g.
9	Ta_2O_5 0·1510	0·0235	1	30 ml.	0·1676
10	,, 0·2042	0·0240	1·2	25 ,,	0·2047
11	,, 0·2020	0·0232	2	equal bulk	0·2020
12	Nb_2O_5 0·2020	0·0234	2	,, ,,	0·1952
13	,, 0·2046	0·0253	2	,, ,,	0·2203

This procedure gave a serviceable tantalum, but low niobium, recovery. In Exp. 13 we precipitated the niobium in half-saturated ammonium chloride solution, but neutralised the solution completely after addition of tannin in the manner described for "Zirconia and Titania."[8] The resultant niobium precipitate was now strongly contaminated with ceria.

We may conclude that the interval between complete tantalum and incipient cerium precipitation appears to be wide enough to render their separation possible. On the other hand, complete precipitation of niobium was not achieved in our experiments without extensive co-precipitation of cerium. We doubt whether tannin could achieve a quantitative separation of the rare earths from the earth acids without recourse to a process of fractional precipitation.

D. Behaviour in Tartaric Hydrolysis.—In Section XVI[12] four experiments were made on tartaric hydrolysis of the earth acids in presence of thoria; it was found that the precipitates, *HP*, occluded thoria. In two tests made with "ceria earths of unknown purity," no co-precipitation could be observed. The present sub-section is a continuation of the earlier work, which was suspended for want of pure rare-earth preparations.

Our experiments (19 and 20) confirmed the co-precipitation of thoria. In the final series of tests, reproduced below, we definitely proved the precipitated earth

acids to be free from rare earths. The bisulphate melt of the mixed oxides was dissolved in 50 ml. of 8 per cent. tartaric acid solution, the solution (300 ml.) was boiled with 30 ml. of strong hydrochloric acid, the precipitate HP^1 was collected, returned to the beaker, and well churned up with filter-pulp and wash-liquor for the complete removal of any soluble rare-earth salts; the precipitate was then returned to the filter, and the washing concluded as usual. The precipitate was ignited, and submitted to the same sequence of operations. The products were a second precipitate, HP^2 (which was discarded), and the filtrate therefrom, containing any rare earth occluded in HP^1, together with the few mg. of earth acid that normally escape precipitation. The oxides in these filtrates were recovered by precipitation with tannin and excess of ammonia (as under C above), and the small precipitate, TP^2, was ignited and weighed.

The filtrate from HP^1, containing the rare earths and a few mg. of earth acid, was treated with tannin and ammonia exactly as the filtrate from HP^2. This gave a precipitate, TP^1, in which the rare earth was determined by the two methods discussed under A and B above.

(A) *By Pied's procedure, i.e.* ignition, bisulphate fusion, extraction of the melt with 5 per cent. oxalic acid, and filtration after standing overnight (Exps. 14 to 20). The filters containing the insoluble oxalates were treated with nitric and sulphuric acids for the destruction of organic matter; the residual acid was diluted and filtered, the filtrate treated with ammonia, and the precipitate ignited and weighed.

	Taken				Rare earth	
Exp.	M_2O_5 g.	Rare earth g.	TP^1 g.	TP^2 g.	in TP^1 g.	Error g.
14	Ta_2O_5 0·2052	CeO_2 0·0211	0·0251	0·0027	0·0200	−0·0011
15	Nb_2O_5 0·2037	,, 0·0220	0·0366	0·0108	0·0216	−0·0004
16	Ta_2O_5 0·2022	Y_2O_3 0·0234	0·0298	0·0025	0·0225	−0·0009
17	Nb_2O_5 0·2013	,, 0·0217	0·0366	0·0084	0·0220	+0·0003
18	Ta_2O_5 0·2026	Nd_2O_3 0·0207	0·0264	0·0022	0·0212	+0·0005

The small precipitates TP^2 were tested for rare earths by fusion with bisulphate and extraction with oxalic acid on a small scale. Such a procedure constitutes a delicate test, but nevertheless it failed to detect any rare earth in the precipitates. What remained insoluble after the extraction weighed a fraction of a mg. and proved to be silica, the usual impurity in tannin precipitates produced in ammoniacal solutions.

In Exps. 19 and 20 we proved the co-precipitation of thoria in tartaric hydrolysis by using the above procedure.

	Taken					
Exp.	M_2O_5 g.	ThO_2 g.	TP^1 g.	ThO_2 in TP^1 g.	TP^2 g.	ThO_2 in TP^2 g.
19	Ta_2O_5 0·2028	0·0239	0·0261	0·0184	0·0065	0·0034
20	Nb_2O_5 0·2048	0·0223	0·0340	0·0197	0·0131	0·0022

(B) *By oxalate precipitation from tartrate solution, i.e.* ignition, fusion with a minimum of *sodium* bisulphate, solution of melt in tartaric acid and filtration to remove silica; precipitation of hot solution (about 50 ml.) with oxalic acid during agitation; filtration next day, and cautious ignition of oxalate to oxide.

Method B was suggested by Mr. H. F. V. Little as an alternative to A. On the whole, we give preference to Method B; it certainly saves time and labour. We noticed one slight disadvantage, *viz.* that the clear filtrate from the oxalate precipitate, *OP*, on being mingled with the oxalic-acid washings, almost invariably deposited a further small crop of crystals yielding a mg. or less of rare earth; this was collected separately. The figures given under *OP*, Exps. 21 to 28, represent the combined weights of the ignited oxalate precipitates:

Exp.	Taken		*TP*	*OP*	Rare-earth error
	M_2O_5	Rare earth			
	g.	g.	g.	g.	
21	Ta_2O_5 0·2018	CeO_2 0·0224	0·0274	0·0219	−0·0005
22	Nb_2O_5 0·2010	,, 0·0247	0·0377	0·0252	+0·0005
23	Ta_2O_5 0·2058	,, 0·0251	0·0308	0·0243	−0·0008
24	Nb_2O_5 0·2054	,, 0·0219	0·0404	0·0217	−0·0002
25	Ta_2O_5 0·2020	Y_2O_3 0·0234	0·0300	0·0231	−0·0003
26	Nb_2O_5 0·2022	,, 0·0230	0·0370	0·0235	+0·0005
27	Ta_2O_5 0·2048	Nd_2O_3 0·0284	0·0360	0·0272	−0·0012
28	Nb_2O_5 0·2024	,, 0·0250	0·0394	0·0245	−0·0005

E. ANALYTICAL APPLICATION.—The above combination of procedures, *viz.* (α) tartaric hydrolysis (single precipitation), (β) tannin precipitation from ammoniacal tartrate solution, and (γ) extraction of the bisulphate melt of the ignited tannin precipitate with oxalic acid solution or precipitation of the oxalates from tartrate solution—either procedure on a small scale—forms what we consider the most reliable means for the determination and identification of small quantities of rare earths in earth-acid minerals. Tartaric hydrolysis eliminates the earth acids (all but a few mg.) as a precipitate free from rare earths, the non-precipitated earth acid acting as a collector in the subsequent tannin precipitation if the rare earths are very subordinate.

The new process effects a far better separation than the obsolete pyrosulphate hydrolysis method,[5] in which the insoluble earth-acid residue from the extraction of the bisulphate melt retains appreciable quantities of other earths.

The ignited rare earths should, of course, be tested for thoria. A more complex separation case affecting the rare earths as mineral associates of the earth acids has yet to be investigated, *viz.* the separation of small amounts of rare earths from the pentoxide and dioxide earths.

SUMMARY.—For the separation of large quantities of rare earths from the earth acids, J. L. Smith's hydrofluoric acid method is considered to be the best. The application of our tartaric acid scheme to the soluble fluoride fraction obtained in Smith's method is an improvement on the original procedure.

Certain processes for the separation of small amounts of rare earths from much earth acid were studied. (1) Pied's proposed method (extraction of a bisulphate melt with oxalic acid solution) is not to be recommended except on a centigram scale. (2) The direct precipitation of the oxalates from a tartrate solution containing much earth acid is not suitable for the recovery of the rare earths; on a small scale, however (*i.e.* with 2 cg. or less of pentoxide), the method is quite satisfactory. (3) Tannin quantitatively precipitates the rare earths from ammoniacal tartrate solution; the precipitates are readily soluble in acetic acid. Tannin precipitation from feebly acid tartrate solution does not effect a clean-cut

separation of the rare earths from the earth acids. (4) When the earth acids are precipitated by tartaric hydrolysis, the precipitate is quite free from rare earths. (5) We recommend the following separation process: precipitation of the bulk of the earth acids by tartaric hydrolysis, recovery of the rare earths and the balance of the earth acids by tannin precipitation from the ammoniacal filtrate, fusion of the ignited small tannin precipitate with bisulphate, and extraction of the melt with oxalic acid solution, or solution of the melt in tartaric acid and precipitation of the rare earths with oxalic acid.

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A New Volumetric Method for the Determination of Beryllium*

BY B. S. EVANS, M.C., D.Sc., F.I.C.

BERYLLIUM, in spite of its high price, is being increasingly used as a component of certain alloys, notably those containing copper. The process which is the subject of this paper was originally worked out to provide a method for its determination in a series of beryllium-lead alloys; although it was subsequently found that beryllium does not appear to mix with lead, this does not detract from any value the process itself may have.

The process is based primarily on the very low equivalent weight of beryllium (4·51), which causes it to combine with a relatively large amount of acid; hence, if it can be made to act as an alkali which can be titrated with standard acid, the conversion factor, acid consumed: beryllium, is very low, instead of being, as in the case of most metals, unmanageably high; thus:

1 ml. of $N/10$ acid ≡ 0·00045 g. of beryllium
,, ,, ,, ≡ 0·00327 g. of zinc

Added to this are the facts that beryllium salts are, momentarily, not precipitated by an iodide-iodate mixture and that they are soluble in sodium bicarbonate solution, thus rendering possible an iodimetric titration of the excess of acid added.

Details of the process are as follows:—The beryllium, after having been freed from other metals having insoluble hydroxides, is precipitated with ammonia and filtered. The precipitate is dissolved through the filter with 20 ml. of dilute (1 : 1) hydrochloric acid, and the filter is washed with water. About 1 ml. of 0·04 per

* Communication from Research Department, Woolwich.

cent. thymolphthalein solution is added to the filtrate, followed by sodium hydroxide solution until the liquid is dark blue, and then by dilute (1 : 1) hydrochloric acid, drop by drop, until it is again colourless, about 3 drops being added in excess. The solution is now boiled vigorously for ten minutes, after which 2 per cent. solution of sodium hydroxide is added, a few drops at a time, until the liquid becomes a darkish blue, too large an excess being avoided; boiling is then continued for another ten minutes. At the end of this time the blue colour is exactly discharged by titrating the boiling solution with $N/10$ hydrochloric acid; this operation demands care, the colour at the end being faint and only slowly discharged; it is desirable when the colour becomes doubtful to allow the precipitate to settle and to look through the clear liquid at a white tile held diagonally to a window; the first part of the titration should be carried on until the colour is faint and the solution then again heated to boiling before finishing it, drop by drop. A measured excess of $N/10$ hydrochloric acid is next added (the total volume at this point should be at least about 200 ml.; if not, water must be added). The solution is boiled for 1 minute and then cooled; when it is quite cold, 20 ml. of saturated potassium iodate solution are mixed with 20 ml. of 4 per cent. potassium iodide solution and immediately added to it, and the flask is vigorously swirled for 2 or 3 seconds (not longer); about 4 grams of solid sodium bicarbonate are dropped in, the flask is again swirled and the liberated iodine at once titrated with $N/10$ arsenious oxide solution in the ordinary way. The arsenious oxide solution for this titration must not contain free acid; it is made up by dissolving the correct weight of arsenious oxide in sodium hydroxide solution, diluting, acidifying and finally adding an excess of sodium bicarbonate, thoroughly shaking to remove carbon dioxide and diluting to the required volume. The operations from the addition of the iodide-iodate mixture to the end of the titration must be carried through with a minimum of delay. The hydrochloric acid is standardised against the arsenic solution by treating with iodide-iodate mixture and titrating the liberated iodine in the same way. The number of ml. of $N/10$ arsenious oxide solution required for the titration of the sample, deducted from the number required for titrating the measured excess of $N/10$ acid originally added, gives the number of ml. of $N/10$ hydrochloric acid neutralised by the beryllium hydroxide, and this, multiplied by 0·00045, gives the weight in grams of beryllium present.

Experimental determinations of beryllium were carried out by this method, with the following results:

Added g.	≡ ml. of $N/10$ HCl	Titration (ml. $N/10$ As_2O_3)	Found g.
0·01038	23·05	35·00 − 11·95 = 23·05	0·01038
0·00934	20·75	29·80 − 9·05 = 20·75	0·00934
0·00831	18·45	29·80 − 11·40 = 18·40	0·00828
0·00727	16·15	29·80 − 13·75 = 16·05	0·00722
0·00623	13·85	29·80 − 15·70 = 14·10	0·00635
0·00519	11·55	29·80 − 18·10 = 11·70	0·00526
0·00415	9·22	29·80 − 20·65 = 9·15	0·00412
0·00311	6·91	19·90 − 12·85 = 7·05	0·00317
0·00207	4·60	19·90 − 15·25 = 4·65	0·00209
0·00104	2·31	19·90 − 17·45 = 2·45	0·00110

Separation of beryllium from a large amount of lead was achieved as follows:

Quantities of 10 g. each of lead were dissolved in nitric acid, and varying amounts of beryllium were added; 20 ml. of dilute (1 : 3) sulphuric acid were added to each, and the resulting precipitates, after cooling, were filtered off and washed with 2 per cent. sulphuric acid. The filtrates and washings were made alkaline with sodium hydroxide and then neutralised with dilute (1 : 3) sulphuric acid, 2 to 3 ml. excess being added; about 4 g. of sodium bicarbonate were next dropped in cautiously, a little at a time (if a scrap of litmus paper floating in the liquid was not now of a bluish shade more bicarbonate was added), and a rapid stream of hydrogen sulphide was passed for 40 seconds, after which the flasks were left on the steam-bath for about 20 minutes, with occasional agitation. The precipitated lead sulphide was filtered off and washed with hot sodium chloride solution (5 per cent.); the filtrate was made strongly acid with hydrochloric acid and boiled for a few minutes; the sulphur cloud was dispelled by the addition of a solution of bromine in hydrochloric acid, and the excess of bromine was boiled out. After addition of 20 ml. of ammonium chloride solution (20 per cent.) to the filtrate the beryllium was precipitated with ammonia, the liquid was boiled for a minute or two, and the beryllium hydroxide was filtered off and washed with hot ammonium chloride solution (5 per cent.). This precipitate was treated as described in the earlier part of the paper, and the volumetric determination was carried out. The results were as follows:

Lead taken g.	Beryllium added g.	≡ ml. N/10 HCl	Titration (ml. of N/10 As_2O_3)	Beryllium found g.
10·0	0·01038	23·05	29·80 — 6·75 = 23·05	0·01038
10·0	0·00831	18·45	29·80 — 12·00 = 17·80	0·00801
10·0	0·00623	13·85	19·85 — 6·30 = 13·55	0·00610
10·0	0·00415	9·22	19·85 — 10·70 = 9·15	0·00412
10·0	0·00207	4·61	19·85 — 15·05 = 4·80	0·00216

The only part of the volumetric determination which is at all troublesome is the exact neutralisation of the solution with $N/10$ hydrochloric acid, as the colour-change is gradual and very slight; as an offset against this, however, is the very low factor of the beryllium, an error of as much as 1 ml. corresponding to less than 0·5 mg. of beryllium.

Traces of aluminium and iron do not seem to interfere with the titration, but larger amounts must be separated.

The Determination of Traces of Cyanides in Water

By A. E. CHILDS, B.A., B.Sc., and the late W. C. BALL, D.Sc., M.A., F.I.C.

In a recent research[1] into the causes of the high mortality of fish in certain rivers there were early indications that one of the chief factors was the presence, in the water, of cyanides—arising from the discharge of various industrial effluents into the stream. As cyanide compounds are highly toxic to fish—concentrations as low as 0·1 to 0·3 parts per million being poisonous—a method of determining very small quantities of cyanides was essential.

There is a considerable volume of literature on the subject, but, as opinions are somewhat conflicting as to the relative sensitiveness of the various tests, a critical examination was undertaken to determine which of them would be most suitable for the purpose in question.

The tests described in the literature generally give good results with aqueous solutions of pure hydrocyanic acid or readily decomposed cyanides. Many of the tests, however, are not specific, the precipitations or changes in colour upon which they depend being given equally well by other substances, or, in some cases, being inhibited or masked by the presence of impurities.

In testing for cyanides, therefore, in river or other crude waters, it is inadmissible in most cases to apply the tests to the water direct. The impurities must, as far as possible, be removed. This is best achieved by preliminary distillation of the water, the determination of the cyanide being made subsequently on the distillate.

Preliminary Preparation of the Sample.—A known volume of the water to be tested (500 ml. is a convenient quantity) is placed, after filtration from suspended matter, in a round-bottomed flask, fitted with a Liebig condenser. Tartaric acid (0·5 g.) is added to the water, which is then gently distilled, a few fragments of porous pot being added to prevent bumping. Should the sample of water be originally alkaline, it must first be neutralised with tartaric acid, and the 0·5 g. of acid then added.

Hydrocyanic acid is readily volatile in steam and 95 per cent. or more of the cyanides (if readily decomposable) present in the water will be found in the first 25 ml. of the distillate. It is advisable, however, to collect 50 ml. Even then, a small trace of cyanide, which experiment has shown not to exceed 1 per cent. of the amount originally present, still remains in the distillation flask. Should the concentration of cyanide be less than 1 in 10 millions, only 25 ml. of the distillate should be collected. The small loss thus introduced is more than counterbalanced by the greater accuracy obtained in the subsequent determination.

The distillate should be colourless and free from opalescence. If this is not the case, the presence of steam-volatile impurities (*e.g.* phenols, fatty acids, etc.) must be suspected.

As these impurities interfere somewhat with several of the tests described later, it is advisable, if their presence is suspected, to carry out the distillation under reduced pressure and at as low a temperature as practicable. By this means the amount of them found in the distillate will be reduced. It should be borne in mind that, in carrying out this distillation under reduced pressure, a very efficient condenser is required.

Chlorides, bromides, iodides, ferrocyanides, ferricyanides, cyanates, thiocyanates, chromates, and non-volatile substances generally, which may be present in the water under examination, will not be found in the distillate.

If sulphides are present in the water, hydrogen sulphide may be found in the distillate, and will tend to interfere with certain of the tests. If this should be the case, a very slight excess of lead nitrate or acetate solution may be added to the water before the addition of tartaric acid and the lead sulphide produced filtered off before distillation. The addition of the lead salt will cause no loss of cyanide (as lead cyanide) provided that the concentration of cyanide in the water does not exceed 1 part in half a million.

The presence of a sufficiency of a strong oxidising agent in the water may tend to oxidise some of the cyanide to cyanate, which would cause the results obtained from the distillate to be somewhat low.

In the presence of ferrocyanides the results will be high, for distillation of solutions of these compounds with tartaric acid causes the precipitation of ferrous hydrogen ferrocyanide and the liberation of an equivalent quantity of hydrocyanic acid.

After sufficient of the distillate has been collected, it is well mixed and an aliquot part taken for the determination of the hydrocyanic acid therein.

Method of Carrying out the Determination

The method recommended is a colorimetric one and depends upon matching the colour produced when known amounts of cyanide are mixed with various reagents, with that produced by a known volume of the distillate—obtained as described above—treated in an identical manner.

For this purpose a series of thin, colourless, flat-bottomed glass tubes, similar to small Nessler glasses is required. These should be as nearly as possible of the same diameter and should be accurately calibrated to 10 ml. (Those used in these experiments were approximately 7·5 cm. long and 1·8 cm. in diameter, and were obtained from Messrs. Baird & Tatlock, Ltd., London.)

Several of these tubes are taken, and a series of standards is made by placing therein known, gradually increasing, amounts of an accurately standardised solution of potassium cyanide. Sufficient distilled water is then added to bring the volume in each to about 8 ml., and a definite volume of the reagent (generally 1 ml.) is added. The contents of the tubes are then accurately made up to 10 ml. with distilled water and throughly mixed.

At the same time a known volume of the distillate, obtained as already described, is treated in an exactly similar manner.

In order to avoid the preparation of a large number of standards, it is advisable to carry out a preliminary test to determine approximately the amount

of cyanide present, and then to repeat the test, using a more closely graduated series of standards and bracketing the approximate amount found.

When the colour produced by the test is weak, the matching is best carried out by looking through the depth of the liquid in the tubes, against a white background or, in the case of an opalescence, against a dark background. With the more intense colours (produced by greater amounts of cyanide) an optical arrangement similar to that used in the Lovibond Tintometer will be found to be advantageous, as this apparatus not only evenly illuminates the "standard" and the "unknown" under examination, but also permits of a simultaneous view of both.

ANALYTICAL CONSIDERATION OF THE VARIOUS TESTS.—A critical examination was carried out on upwards of twenty tests (including various modifications thereto) that have from time to time been published. Of these, the following four were found to be the most suitable for the determination of small quantities of cyanides in river or crude waters. Two of them [(*c*) and (*d*)] are not specific for cyanides, but are so much more sensitive than the specific tests (*a*) and (*b*) that, for very low concentrations, the use of one of them is almost obligatory.

(*a*) *Prussian Blue Test.*—This test, which is specific for cyanides (in the absence of ferrocyanides), depends upon the formation of a ferrocyanide when an alkaline solution of an easily decomposable cyanide is warmed with a solution of ferrous sulphate. On subsequent acidification with hydrochloric acid and addition of a small quantity of a ferric salt the deep blue colour of Prussian blue is produced. If, however, a considerable quantity of cyanide is present, the Prussian blue is formed as a dense blue precipitate.

Gentle heat promotes the reaction, but too great an excess of alkali or hydrochloric acid must be avoided.

To carry out the determination of cyanides by this test, the following reagents are required:

An approx. 0·1 per cent. aqueous solution of ferrous sulphate (freshly prepared).
" " 0·1 " " " " " ferric chloride.
" " 1·0 " " " " " sodium hydroxide.
" " 1·0 " " " " " hydrochloric acid.

To a known volume (5 to 8 ml.) of the distillate, obtained as described above, 2 drops of the sodium hydroxide solution are added and then 1 ml. of the ferrous sulphate solution. After gentle warming the mixture is allowed to remain for about 5 minutes, when 5 drops of ferric chloride are added, followed by 1 ml. of 1 per cent. hydrochloric acid. The whole is then made up accurately to 10 ml. with distilled water and well mixed.

The determination of the cyanide is carried out by matching the blue colour produced with that from known amounts of cyanide treated in identical manner.

If a blue precipitate is at once produced, the determination, by colour matching, cannot be accurately carried out, so that, should this occur, a smaller quantity of the solution containing the cyanide must be taken and the test repeated.

Though this test is specific for cyanides and is therefore admirable in that respect, it is not, comparatively speaking, very sensitive. Anderson[2] states that 0·04 mg. of hydrocyanic acid in 10 ml. (1 part in 250,000) can be detected by this test, though in this series of experiments the lowest amount that could be detected

was 0·2 mg. in 10 ml. With solutions containing less than 1 part of hydrocyanic acid in 100,000 no reaction was given, irrespective of the volume taken. (This agrees with the later finding of Anderson.[3]) This is probably due to incomplete conversion of the cyanide, at this dilution, into ferrocyanide; since, once Prussian blue has been formed, it can be diluted several times below the concentration limit at which the test, as normally carried out, fails.

The Prussian-blue test, rather than any other, should be used for the determination of cyanides in crude waters, if the concentration therein is not less than 1 part of hydrocyanic acid in 250,000.

(*b*) *Thiocyanate Test.*—This test, in the absence of thiocyanates, is also specific for cyanides. It was found to be about 5 to 10 times as sensitive as the Prussian-blue test.

It is, however, somewhat complicated and tedious to carry out, and at extreme limits of dilution did not prove very reliable. Its use is not recommended.

(*c*) *Silver Cyanide Test.*—This test depends upon the opalescence produced when excess of silver nitrate is added to a slightly acid solution of a cyanide. It is not specific for cyanides, as halogen acids and their salts and certain fatty acids also produce an opalescence with silver nitrate. Sulphides and free hydrogen sulphide interfere by precipitation of the silver.

If the sample of the crude water is subjected to preliminary distillation, no halogen salts or acids can be found in the distillate, unless sufficient oxidising agents are also present to liberate the free halogens. This, however, is extremely unlikely to occur in river water. Stearic acid (and allied compounds) may, however, be found in the distillate and, if present, will interfere with the test by producing an opalescence. Phenolic substances, if present in amounts smaller than that necessary to produce a turbidity in the distillate (before the addition of silver nitrate), do not interfere, though, if this amount is exceeded, they naturally will.

To carry out this test the following reagents are required:—$N/10$ silver nitrate solution; 1 per cent. nitric acid; 1 per cent. ammonia.

To a known volume of the distillate obtained from the water under examination, 5 drops of ammonia and then 3 drops of silver nitrate solution are added. (The presence of the ammonia was found to increase the sensitivity of the test for hydrocyanic acid, though Anderson[2] states the contrary.) This is then acidified with 1 ml. of nitric acid, made up accurately to 10 ml. with distilled water (chloride-free) and well mixed.

The determination of the cyanide present is carried out by matching the opalescence produced with that from known amounts of cyanide.

The limiting concentration at which the opalescence produced by this test can be detected is 0·005 mg. of hydrocyanic acid in 10 ml. of water, *i.e.* 1 part in 2,000,000. With concentrations of 0·02 mg. in 10 ml. (1 part in 500,000) the opalescence is readily distinguishable.

When 500 ml. of the water are distilled in the manner described, this test allows of the detection of 1 part in 5 millions. For concentrations of this order it would appear to be a very reliable method.

(*d*) *Phenolphthalin Test* (Weehuizen's test[4]).—This is a very sensitive test,

and, if proper precautions are taken, it can be used for the determination of extremely dilute solutions of cyanides.

It depends for its action on the production of a red colour by the oxidation, in the cold, of an alkaline solution of phenolphthalin to phenolphthalein in the presence of a cyanide and a weak solution of a cupric salt.

It is, however, not specific for cyanides, as other compounds which are able to oxidise the phenolphthalin under these conditions will also give a positive reaction.

To carry out the test, the following reagents are required:—A 0·3 per cent. aqueous solution of copper acetate; 2·5 per cent. aqueous solution of glycerin; 1 per cent. sodium hydroxide solution; and a 1 per cent. aqueous solution of phenolphthalin containing 20 ml. of 1 per cent. sodium hydroxide solution per 100 ml.

It is essential that the phenolphthalin should be of a high order of purity and free from phenolphthalein. That used in these experiments was obtained from The British Drug Houses, Ltd.

To prepare the actual reagent for the test, 10 ml. of the above phenolphthalin solution are diluted to 50 ml. with 2½ per cent. glycerin solution. To this are added 50 ml. of 0·3 per cent. copper acetate solution, and the whole is well mixed, filtered (if cloudy) and kept in a stoppered glass bottle. (The function of the glycerin is to prevent the precipitation of the copper as hydroxide on the subsequent addition to it of caustic soda. It also increases considerably the sensitivity of the test.)

The estimation is carried out by taking a known volume of the solution containing the cyanide and adding to it 1 ml. of the above mixed reagent. Five drops of a 1 per cent. caustic soda solution are then added and the whole is made up accurately to 10 ml. with distilled water and well mixed. The temperature should not be allowed to exceed 15° C.

The amount of cyanide is estimated by matching the reddish colour produced with that obtained from known amounts of cyanide.

Though the colour produced by the test is fairly lasting, it does change with time, so that the matching should be carried out with the minimum of delay.

As mentioned above, the test is not specific for cyanides. Ferricyanides and aqueous solutions of the halogens give a similar coloration. On the other hand, ferrocyanides, chromates, nitric acid, ferric chloride and halogen salts give no reaction, and neither does a weak solution of hydrogen peroxide. One ml. of hydrogen peroxide (20 vols.) diluted to 10 ml. with water does, however, give a slight brownish colour.

Sulphides interfere by precipitating the copper in the reagent, and if present, should be removed from the water before distillation, by the addition of lead nitrate or acetate.

If the sample tested is prepared by distillation of the crude water as described above, no non-volatile impurities will be found in the distillate.

Of the steam-volatile impurities which might be present, fatty acids do not interfere, but phenols, if present in concentration greater than 1 part in 50,000 of the crude water, prevent the full development of depth of colour produced by the cyanide.

The phenolphthalin test gives a faint, but nevertheless perceptible, colour with 0·0005 mg. of hydrocyanic acid in 10 ml. of water (1 part in 20 millions), whilst with 0·002 mg. in the same volume of water the colour produced is quite definite.

Provided that the proper precautions are carried out and that the cyanide present in the crude water is concentrated tenfold by distillation, as described above, this test will give reliable results for the determination of cyanides in concentrations as low as 1 part in 50 millions of the crude water.

The methods recommended for the determination of concentrations of cyanides of the order of one in five millions and lower, are the phenolphthalin and the silver nitrate tests.

With the proper precautions, either of these tests is capable of giving results of a high order of accuracy.

Dr. B. A. Southgate of the Marine Biological Association, who has used these tests in his researches on the estuary waters of the River Tees, has found them reliable and accurate. Duplicate analyses made by him of the cyanide in estuary water taken from the neighbourhood of industrial outfalls gave the following results:

	Cyanogen in g. per 10^6 ml.									
Silver nitrate method	0·55	0·1	0·25	0·65	0·3	0·15	0·05	0·2	0·2	0·4
Phenolphthalin ,,	0·6	0·1	0·2	0·6	0·35	0·1	0·05	0·2	0·3	0·3

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CHEMICAL DEFENCE EXPERIMENTAL STATION
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The Effect of Grinding in a Power Mill on the Albuminoid Content of Feeding Stuffs

BY F. ROBERTSON DODD, F.I.C., AND C. ROBERTSON LOUDEN, B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, December* 8, 1934)

IN THE ANALYST for September (1934, p. 606) Dr. F. J. Elliott, writing "Notes on the Grinding of Feeding Stuffs in a Power Mill," gives figures relating to decorticated ground-nut cake which purport to show that the preparation of a sample for analysis in such a mill is liable to produce an appreciable loss of albuminoids. Since this is a matter of considerable importance to merchants as well as to analysts, experiments were conducted in our respective laboratories on commercial specimens of feeding stuffs.

The Christie & Norris laboratory mill—which Dr. Elliott described—is in use in both laboratories, but without the balloon attachment. In one case the ground powder is received in a canvas bag tightly sewn on to the sieve; in the other, the box drawer supplied with the machine is used as the receiver.

The 1-mm. sieve prescribed in the Official Regulations was used in each case, and the grinding was continued only until all the sample had passed through the

sieve. Three samples were prepared from a ground-nut cake and a cottonseed cake, respectively, one, in each case, being ground by the Christie & Norris machine, one by a cone mill (the Whitmee), and one by mortar and sieve.

The moisture was determined in each sample, with the object of ascertaining whether there were any appreciable differences on this point in the three modes of grinding.

The following are the figures obtained:

Ground-nut cake	Whitmee mill Per Cent.	Christie & Norris mill (with bag receiver) Per Cent.	Mortar and sieve Per Cent.
Loss in weight ..	0·36	1·7	0·56
Moisture	8·45	8·35	8·20
Albuminoids ..	47·38	47·44	47·31
Cottonseed cake			
Loss in weight ..	0·30	1·0	0·30
Moisture	9·25	9·15	9·35
Albuminoids ..	38·69	38·44	38·75

A series of thirty experimental runs conducted by members of the staff on various types of cakes, in the machine fitted with the box receiver, as in everyday practice, *i.e.* without taking any extra precautions to avoid loss of the dust, showed that samples of 100 g. in weight, when passed through the Christie & Norris machine, might lose between 2 and 3 g.

The following figures for albuminoids, actually obtained in the course of routine control work, for seventeen different cakes, compared with those of samples prepared from the same bulks by grinding in a hand-mill, are instructive:

		Hand-mill		Christie & Norris mill	
		Albuminoids Per Cent.	Moisture Per Cent.	Albuminoids Per Cent.	Moisture Per Cent.
Ground-nut cake	No. 1	42·8	—	42·8	—
,, ,,	No. 2	44·0	8·0	43·9	8·2
,, ,,	No. 3	44·4	8·4	44·6	8·6
Cottonseed cake	No. 1	44·6	8·0	44·5	8·0
,, ,,	No. 2	44·2	8·6	44·4	8·6
,, ,,	No. 3	43·1	11·0	42·9	11·2
Soya-bean meal	No. 1	45·8	12·4	45·7	12·2
,, ,,	No. 2	46·7	10·8	46·8	11·0
,, ,,	No. 3	47·8	12·0	48·0	11·8
Linseed cake	No. 1	31·5	9·2	31·4	9·2
,, ,,	No. 2	33·8	8·8	34·0	9·0
,, ,,	No. 3	34·2	8·8	34·1	8·8
,, ,,	No. 4	33·5	8·4	33·6	8·8
Ground-nut meal	No. 1	55·5	—	55·4	—
,, ,,	No. 2	55·8	—	55·7	—
Rape meal		35·5	7·6	35·7	7·6
Pollards		16·5	12·2	16·3	12·2

We refrain from detailed comment on Dr. Elliott's figures, which, on the assumption of 3·6 per cent. loss in milling—his figure for hay—appear to indicate that the balloon attachment exercises a selective power on the albuminoid content, and causes the dispersion of matter containing over 100 per cent. of albuminoids.

The Influence of Amyl Ether on the indicated Fat-Percentage in the Gerber Process

A New Test for the Suitability of Amyl Alcohol

By D. O'SULLIVAN, M.Sc., F.I.C.

This investigation arose out of the difficulties of a creamery with its supplies of amyl alcohol (for milk analysis) bought in the usual way in the spring of 1933. The first sign of trouble was the indication of 0·18 per cent. of fat in the skimmed milk, a reasonable anticipation being reduction to an indication of 0·05 per cent. or less for machines running well. The Gerber test, applied to machine-skimmed milks, cannot be expected to give strictly accurate results, but its indications can form a useful check on the working of the separators.

Preliminary Examination.—The alcohol in question had the following characteristics:—(i) Sp.gr. at 15·5° C., 0·814. (ii) Ten ml. with 10 ml. of hydrochloric acid (sp.gr. 1·16) gave a clear solution; the addition of 1 ml. of water caused a separation. (iii) Two ml., when dissolved in 20 ml. of cold 50 per cent. (by vol.) sulphuric acid and centrifuged, showed no oily layer or globules.

The results obtained in the Gerber process, with 1 ml. of amyl alcohol, from used and unused packages of the same creamery supply were compared with the result given by the laboratory stock alcohol, and with the fat-percentage determined in the same milk by the Röse-Gottlieb process, and the following results were obtained:

	Fat Per Cent.	Excess Per Cent.
Used	3·05	0·15
Unused	3·05	0·15
Laboratory-stock alcohol ..	2·9	Nil
Röse-Gottlieb	2·9	—

A separation of the interfering constituents by distillation was next attempted, a Le Bel and Henninger fractionating column being used. The various fractions were applied to the determination of fat by the Gerber process in another sample of milk, 1 ml. being used. Fifty ml. were distilled, and six distillates were collected in succession, each measuring about 7 ml.

	Fat Per Cent.	Excess Per Cent.
1st Fraction	3·5	0·05
2nd ,, ...	3·55	0·10
3rd ,, ...	3·5	0·05
4th ,, ...	3·5	0·05
5th ,, ...	3·6	0·15
6th ,, ...	3·7	0·25
Residue	3·9	0·45
Laboratory-stock alcohol ..	3·45	—

The reduction of the excess obtained in the Gerber process with the first four fractions, and its rise in the 5th and 6th fractions and the residue, indicated a method for the concentration of the undesirable constituents. A further sample

(about 1½ l.) of the alcohol was, therefore, procured. With the Gerber test it gave the following result:

	Fat Per Cent.	Excess Per Cent.
This alcohol	3·6	0·2
Laboratory-stock alcohol ..	3·4	—

First Fractionation.—Five hundred ml. were distilled, a 4-bulb Le Bel and Henninger fractionating column being used, and fractions were collected until 400 ml. had passed over.

The various fractions and the residue were then tested by the Gerber process. (All temperatures are roughly corrected for the length of the emergent stem of the thermometer.)

Ml.	Boiling point °C.	Fat Per Cent.	Excess Per Cent.
0–100	124–131	3·5	0·1
100–200	131–131·5	3·5	0·1
200–300	131·5–131·5	3·5	0·1
300–400	131·5–132	3·55	0·15
Residue in flask	132–	3·75	0·35
Laboratory-stock alcohol		3·4	—

The residue was now distilled slowly through the fractionating column, and smaller fractions were collected:

Ml.	°C.	Fat Per Cent.	Excess Per Cent.
400–425	130·5–131·5	3·75	0·15
425–450	131·5–131·5	3·8	0·2
450–475	131·5–132	3·85	0·25
475–490	132–132	3·9	0·3
490–496	132–132·5	4·0	0·4
Residue		4·8	1·2
Laboratory-stock alcohol		3·6	—

The concentration of the undesirable constituent in the later fractions was here apparent.

The final residue was further examined as follows:

For fat: A drop placed on filter-paper evaporated completely in the air without leaving a stain. There was, therefore, no fat or oil present.

Acid value and Ester value.—For comparison, the acid value and ester value of the laboratory stock alcohol were also determined.

	Residue	Laboratory stock	Blank
Acid value	g.	g.	
Weight taken	1·33	1·33	—
$N/10$ sodium hydroxide solution, ml. ..	0·2	0·03	—
Acid value	0·8	Nil	—
Ester value	25 ml. of approximately $N/2$ alcoholic potash were now added, and the mixture was boiled under a reflux condenser for 30 minutes and titrated with $N/2$ hydrochloric acid.		
$N/2$ hydrochloric acid, ml.	22·11	22·18	22·22
Ester value, as amyl acetate	0·005	Nil	—

In the case of the residue, the titrated liquor was quite cloudy and threw up oily drops having an odour of pears. The figures have no positive significance,

but indicate the presence of ethers, aldehydes or their variations, rather than esters.

Test for aldehydes.—The residue gave no reaction with Schiff's reagent or ammoniacal silver nitrate solution.

Test for nitrogen and sulphur compounds.—The residue was boiled down with metallic sodium and then charred and tested in the usual way. There was no reaction.

Test for halogens.—These were not present.

The presence of an ether, probably amyl ether, was therefore suspected, and on this assumption a second fractionation of the original was undertaken. Five hundred ml. were used, and the Le Bel-Henninger column was replaced by the more efficient Sydney Young type, lagged.

Second Fractionation.—The first fraction, boiling at 95° to 100° C., amounted to 4 ml., and consisted of two layers, which were separated. The upper layer gave the Schiff reaction for aldehydes, and had b.p. 101° C.

Mixed with laboratory-stock amyl alcohol to the extent of 10 per cent., it did not interfere in the Gerber process; thus:

	Fat in milk Per Cent.	Excess Per Cent.
Ten per cent. solution of upper layer of fraction in amyl alcohol	2·85	Nil
Laboratory-stock alcohol	2·85	—

It was probably an aldehyde. The lower layer was water.

Second Fractionation continued. Ml.	Boiling-point °C.	Fat in milk Per Cent.	Excess Per Cent.
4–100	130·5–132	2·85	Nil
100–200	132 –132·5	2·85	Nil
200–300	132·5–132·5	2·9	0·05
300–400	132·5–132·5	2·9	0·05
400–480	132·5–132·5	3·1	0·25
Residue	—	—	—
Laboratory-stock alcohol		2·85	

It is to be noted that the fractions from 4 to 400 ml. were fairly satisfactory for use in the Gerber process, and that the amount of the interfering constituent in the distillates was considerably reduced, as compared with the corresponding periods of the first fractionation, owing, presumably, to the more efficient scrubbing of the vapours in the Sydney Young column.

As it did not appear probable that a complete separation of the interfering constituent concentrated in the high-boiling residue in a form suitable for identification could be attained by fractional distillation alone, experiments were made with a mixture of commercial amyl ether and laboratory-stock amyl alcohol to devise a process of isolation. The amyl ether used was described by the makers as "a mixture of isomers of which iso-amyl ether is the chief." (No attempt has been made in this work to distinguish between the various isomeric alcohols and ethers.) Gerber cream-tubes were used. The first attempts at extraction of the amyl ether in amyl alcohol solution by mixing with cold 50 per cent. (by vol.) sulphuric acid and (*a*) olive oil, or (*b*) petroleum spirit (b.p. 40–60° C.) were not successful. Melted, filtered butter-fat gave a satisfactory and clean separation,

as was shown by the increase in its volume when read against the scale of the cream-tube, but this separation was not quantitative.

The residue from the second fractionation was, therefore, treated as follows: Sufficient melted butter-fat to cover about 50 small divisions on the scale (10 divisions = 0·556 ml. of water, when measured cold) was poured into a Gerber cream-tube. Cold 50 per cent. (by vol.) sulphuric acid was added, and then 2 ml. of the residue. The whole was heated gently so as to melt the butter-fat, shaken, centrifuged and cooled in order to solidify the fat; the acid liquid was poured into a second cream-tube containing butter-fat, and the process was repeated in this second tube. Each 2 ml. of the residue was treated similarly. The solid-fat extracts were surface-washed with cold 50 per cent. sulphuric acid and then with water, and the fat was melted at a low temperature and transferred to a distillation flask. The combined butter-fat extracts were distilled in steam. The upper layer of the steam distillate, measuring 2·7 ml., was separated and redistilled.

This second distillate had the following characteristics:—Colourless; insoluble in water; soluble in alcohol, ether and petroleum spirit. It had the peculiar odour of amyl ether. Sp.gr. at 15° C., 0·784; n_D^{20}, 1·409; b.p., 170–172° C. These characteristics identify this liquid as amyl ether.

In order to eliminate the possibility that the amyl ether separated above might have been produced during the treatment of the residue with the acid, another portion of the amyl alcohol was subjected to a third fractionation. Five hundred ml. were distilled, a Sydney Young still-head (lagged) being used. By more careful attention to temperature-control, a small residue boiling above 132° C. was obtained; this was steam-distilled. On subsequent dry distillation a small amount (5·1 ml.) of amyl ether was separated. This showed that amyl ether was pre-formed in this alcohol.

An approximate estimate of the amount of amyl ether in the alcohol was made by diluting commercial amyl ether with amyl alcohol until the excess reading in the Gerber test was 0·2 per cent. A 2 per cent. solution of amyl ether gave the desired result.

A 2 per cent. solution of the separated amyl ether in the 100–200° C. fraction of the second fractionation gave an excess-fat reading in the Gerber process of 0·2 per cent., *viz.*:

	Fat Per Cent.	Excess Per Cent.
This 2 per cent. solution ..	4·15	0·2
Laboratory-stock alcohol ..	3·95	Nil
Fraction, 100–200° C. ..	3·95	Nil

The alcohol was, therefore, reported to contain about 2 per cent. of amyl ether, to which was due its disturbing effect in the Gerber process.

TESTS FOR THE SUITABILITY OF AMYL ALCOHOL FOR THE GERBER PROCESS.—A tribute to the trustworthiness of the Gerber process is the small amount of adverse criticism it has evoked since its inception, more especially considering that it is one of the most widely used of every-day chemical tests. Gerber himself had noted that a naked contact between the acid and the alcohol for any length of time gave too high readings for fat percentage, and recommended

admixture in the order: acid, milk, alcohol. This has been standard practice. The variations of the error due to contact of acid with alcohol were investigated by Richmond and O'Shaughnessy.[4]

In 1905 Richmond and Goodson published a note on the incidence and disturbing effect of petroleum,[5] and later in the same year, Richmond published the result of an investigation of the composition of the "fat" separated in the Gerber process.[1] One point is of particular interest: "14·666 g. of the Gerber fat were steam-distilled, and a marked pear-drop odour was noticed in the distillate." Amyl ether has a pear-drop odour.

In 1923 Harvey and Harvey contributed a note on the separation of an oily layer on mixing even satisfactory samples of amyl alcohol with sulphuric acid and water.[6] In 1933 several notes appeared: from Houston,[7] Golding,[2,3] and More[8]—the last quoting van Haarst[9] and Siegfeld.[10]

Golding's experience with normal amyl alcohol,[3] using 1 ml. and the Gerber process, was confirmed, thus:

	Fat Per Cent.	Excess Per Cent.
Normal amyl alcohol ..	4·2	0·45
Laboratory-stock alcohol ..	3·75	—

A large-scale Gerber test was made with the normal amyl alcohol.

To avoid excessive charring, it was necessary to dilute the acid. Twenty ml. of water and 380 ml. of Gerber acid were mixed and cooled; 440 ml. of milk were floated on, and 40 ml. of normal amyl alcohol were added as a third layer. The flask was fitted with an air-condenser, and the contents were well mixed and allowed to cool somewhat, after which 40 ml. of clear butter-fat were added, and the whole was shaken again, transferred to a separator and allowed to stand. The acid layer was run off (an exact separation was not sought), and the fatty layer was transferred to a flask with a little hot water and steam-distilled. The upper layer of the steam distillate, measuring 2·5 ml., was dry-distilled from a small oil-bath. It yielded:

A small fraction—about 5 per cent.—boiling below 100° C., and with the odour of an aldehyde derived from amyl alcohol.

" " " " 10 per cent.—boiling between 100 and 140° C. and smelling of amyl alcohol;

about 2 ml. of a clear liquid, boiling up to 170° C., and having the characteristics of amyl ether, as previously noted.

A sample of unsatisfactory amyl alcohol kindly supplied by Mr. J. Houston of the Department of Agriculture, Northern Ireland, was next investigated. Used in the Gerber test it gave an excess reading of 0·6 per cent. On fractional distillation about 75 per cent. came over below 132° C. The distillate and the residue were used in the Gerber process:

	Fat Per Cent.	Excess Per Cent.
Distillate	4·15	0·65
Residue	3·8	0·3
Laboratory-stock alcohol ..	3·5	—

These results showed that the sample was a different type of alcohol from that received from the Creamery.

A large-scale Gerber test, conducted, as in the experiment described above, with normal amyl alcohol, gave a steam-distillate, measuring 2·1 ml., which separated similarly, on dry-distillation, into fractions.

The laboratory-stock alcohol, treated by this process, gave a steam-distillate of only 0·2 ml., smelling of amyl ether. The indication is that the high results in the Gerber process when using the other two samples were due to the presence of amyl ether in the "fat."

NEW TEST.—As the ordinary "oily impurities" test did not give any oily layer or globules with the alcohols investigated, another procedure has been devised. It has served to distinguish between the laboratory stock alcohol (which gave no layer) and the following:—The Creamery alcohol; the Northern Ireland alcohol; 1 per cent. amyl ether in laboratory-stock alcohol; 0·5 per cent. amyl ether in laboratory-stock alcohol; 0·25 per cent. amyl ether in laboratory-stock alcohol; normal amyl alcohol (as purchased); and unsatisfactory alcohol (kindly sent to me by Dr. W. L. Davies, of the National Institute for Research in Dairying at Reading).

All these gave layers, and in each case, on completion of the test, the smell of amyl ether was noticeable. The test will probably be of general application, depending, as it does, on giving the alcohols the opportunity to be transformed to ethers under approximately the same conditions as in the Gerber test.

Mix equal quantities of Gerber acid (1·820–1·825) and water, cool and adjust to a specific gravity of 1·510 (about 18·6 *N*). Place 20 ml. in a Gerber bottle, add 2 ml. of the sample, insert stopper, mix and centrifuge. No oily layer or globules should appear. Invert the bottle in a beaker, keep it lightly stoppered, and heat in water to 80° C. for approximately 30 minutes. Centrifuge. No oily layer or globules should appear. Add 2 ml. of water, mix, cool and allow the bottle to stand overnight. Centrifuge. No oily layer or globules should appear. (The appearance of an oily layer is always preceded by cloudiness.)

SUMMARY.—Too high readings for fat-percentage in the Gerber process for the analysis of milk have been shown to be due to amyl ether; the ether is preformed in the amyl alcohol, or formed during the reaction, and extracted by the "fat."

The necessity for adding the acid, milk, and alcohol in the order given is emphasised.

The "oily impurities" test is valueless for the detection of amyl ether in amyl alcohol.

A modified procedure is suggested for the selection of suitable alcohol.

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Some Cryoscopic Measurements of Indian Milk

By P. S. MACMAHON, M.Sc., F.I.C., and L. N. SRIVASTAVA, M.Sc.

A report from the Public Analyst's Laboratory, Rangoon (Bunce[1]), included some cryoscopic measurements of the milk of the cow and buffalo. Although the standard Hortvet procedure was not followed, the results indicated that cryoscopic methods were likely to prove a valuable means of solving the special problems of milk analysis peculiar to India and Burma.

In this part of India the chief disturbing factor is the use of buffalo's milk. There is only a small consumption of goat's milk, whereas the buffalo ranks with the cow as a domestic milch animal of the highest economic importance.

In a memoir published by the Government of the United Provinces (Macmahon, Gupta and Mukerji[2]) the comparative results of the analysis of over 1000 samples of the two kinds of milk are tabulated. In that investigation the buffalo milk throughout the seasons was shown to contain, on the average, 7·19 per cent. of fat and 9·43 per cent. of solids-not-fat, whilst, on the other hand, the composition of cow's milk closely approached European standards. The fluctuation in the principal constituents of the milk of individual animals was so wide as to render the imposition of analytical standards almost meaningless. Those ultimately laid down, *viz.* 3·5 per cent. of fat and 8·5 per cent. of solids-not-fat, based upon the lower limits of cow's milk, thus left plenty of scope for watering down the richer buffalo milk to the limiting composition required by the regulations. As the milk sold in these provinces is usually mixed, the analyst, unaware of its origin, is often faced with a problem of unusual difficulty in the detection of adulteration.

We thought it advisable to make some comparative cryoscopic measurements of milk derived from local sources, particularly in view of the differences between the climatic conditions prevailing in the United Provinces and those of Burma.

Some measurements have previously been made in different parts of India: a few with the milk from individual animals by Leather at Pusa in 1915, and some by Stewart and Banerjea[3] at Calcutta, in addition to those by Bunce at Rangoon already quoted.

Stewart and Banerjea found no difference in the average freezing-points of the two milks, and Bunce has proposed a higher limit of −0·550° C. and −0·560° C. for the cow and buffalo, respectively. These investigators did not use the Hortvet apparatus.

The measurements tabulated below were made with this apparatus, and the procedure conformed strictly with that laid down in the A.O.A.C.,[4] due attention being paid to the points frequently emphasised in the comprehensive work of Elsdon and Stubbs.[5]

The mixed-herd samples were obtained from the Military Dairy Farm, Lucknow, under the supervision of the officer-in-charge, and were invariably examined within a few hours of milking, so as to minimise the risk of development of undue acidity, even in the hottest weather. The acidity was checked from

time to time, and found to be negligible for purposes of the test. The apparatus was found to give comparable results throughout the year, in spite of the great range of atmospheric temperature at Lucknow, which varied in this laboratory from 23·1° C. in January to 38·3° C. in June. The only drawback to its routine use is the heavy consumption of ether, especially in the hot months.

The following condensed table shows the results obtained with the milk from mixed herds, and also with the milk of a single animal of each kind milked on the premises:—

Range of freezing-point depression Δ	Number of samples	Average	Average of all samples	Average solids-not-fat Per Cent.
Milk from an individual cow :				
0·545 to 0·549	3	0·547		
0·550 to 0·555	34	0·552	0·552	
0·556 to 0·560	5	0·559		
Milk from mixed-herd cows (about 60 in number) :				
0·545 to 0·549	7	0·548		
0·550 to 0·555	116	0·551	0·551	8·75
0·556 to 0·559	6	0·557		
0·560 to 0·578	5	0·565		
Milk from an individual buffalo :				
0·555 to 0·559	1	0·555		
0·560 to 0·565	32	0·562	0·562	
Milk from mixed-herd buffaloes (about 60 in number) :				
0·555 to 0·559	17	0·558		
0·560 to 0·565	112	0·561	0·561	9·30
0·566 to 0·584	8	0·575		

The mean Δ for cow's milk was found to be 0·551° (as compared with 0·544 found by Elsdon and Stubbs in England) and 0·562° for buffalo milk, results which coincide with the smaller depressions found by Bunce (*loc. cit.*), and were suggested by him as working standards. In all cases the limits of fluctuation are narrower, and display a satisfactory constancy for purposes of application of the freezing-point method in India. We find the same average difference as Bunce between freezing-points of the two kinds of milk, *viz.* 0·01° C., although at a slightly different level. This small difference, representing less than 2 per cent. of added water, thus places in the hands of the analyst an invaluable means of testing milk, especially that of the buffalo when watered down to the "legal" standard. The freezing-point appears to be independent of the widely fluctuating values of the natural constituents of the milks of these two species of animal.

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Liesegang Rings

Methods of Analysis for the Determination of Silver, Chromate, etc., in Gelatin or Agar Gel

By E. B. HUGHES, M.Sc., F.I.C.

(*Read at the Meeting, April* 3, 1935)

Introduction.—At a recent meeting of the Society (April 3rd, 1935) an account was given of an analytical study[1,2] of Liesegang Rings and the theory deduced therefrom. As results of analytical investigations are incomplete without details of the methods employed, and as the methods may also have other applications (for example, the method for chromate in gelatin is equally applicable to the determination of chromium in food materials), the working details of the methods are here given.

Purification of the Gelatin (*For experiments with silver chromate*).—For experiments in which the concentration of silver is so small that the amount of it reacting with salts originally present in the gelatin may be appreciable, it is necessary to employ gelatin in which the chloride, particularly, is low in amount.

(*a*) *Ash-free Gelatin.*—Loeb's[3] method of preparing ash-free gelatin (extraction of mineral matter with 0·0078 *N* acetic acid in the cold) produces gelatin which gives only the faintest qualitative tests for chloride and for phosphate. Unfortunately, in the gel prepared from such gelatin, the solubility of silver chromate is much reduced, and only very poorly formed rings of precipitate can be obtained in it, very little improvement being effected, even when the *p*H of the gelatin is altered (the *p*H of this ash-free gelatin being at about the *iso*-electric point, 4·7); in the preparation of such gelatin there are probably other losses in addition to mineral matter. Gelatin so prepared was, however, useful for certain portions of the work.

(*b*) *Electrolytically Purified Gelatin.*—Electro-dialysis through parchment membrane was found not to be a very satisfactory method, but direct electrolysis of a gel gave gelatin of sufficient purity and of unimpaired quality with regard to ring-formation.

A block of a 10 per cent. gel is prepared in a rectangular jar, so formed as to leave a space at each end between the wall of the jar and the gel. When the gel has set firm these spaces are filled with distilled water, carbon electrodes (previously well-boiled and washed) are inserted, and the gel is submitted to electrolysis, the water being frequently tested and changed. Finally, the gel is melted to render it uniform. By this means the chlorine-content of 10 per cent. gel was reduced from 0·004 *N* to 0·002 *N*, which is low enough to be neglected in the experiments in which 5 per cent. gelatin is employed.

Preparation of Samples for Analysis.—At the conclusion of the diffusion experiment the gel is removed from the tube by inserting a wire in contact with

the glass and rotating the tube so as to free the gel, which is then forced out of the tube by blowing. The length of the gel is measured, and it is then cut into thin slices which are weighed and analysed.

Methods of Analysis

(I) Silver and Chromate.—(*a*) If the amount of silver present in a sample is not less than the equivalent of 1 ml. of 0·05 *N*, the following procedure is satisfactory:

The slice of gel (1 to 5 g.) is dissolved in 5 ml. of 5 *N* nitric acid (cold), and made up to 50 ml.

Silver.—Twenty ml. of this solution, after the addition of a few drops of ether to prevent frothing, are directly titrated with standard ammonium thiocyanate solution (0·1 *N* to 0·02 *N*), with ferric alum as indicator; the gelatin does not interfere. If much chromate ion is present its colour may affect the determination of the end-point, but this can be overcome by reduction of the chromate by a drop or two of saturated sodium sulphite solution.

Chromate.—The usual procedure, as given for chromium in chrome leather (*Allen's Commercial Organic Analysis*, 5th Ed., V, 346), is satisfactory.

Typical Test Result.—

One g. of 5 per cent. gelatin, 0·0544 g. of potassium chromate and 0·0340 g. of silver nitrate.

Found: 0·0549 g. of potassium chromate and 0·0342 g. of silver nitrate.

(*b*) *Chromate*, in small amount, in presence of a considerable excess of silver, *e.g.* 0·002 *N* chromate ion and silver up to normal.

The method is based on that of Evans[4] for the determination of chromium in steel, using Cazeneuve's[5] reagent (diphenylcarbazide), and, as given here, is applicable to the determination of chromium in organic matter,* allowing of the measurement of 0·2 p.p.m. of chromium in 5 g. material; consequently the method is described in full detail.

The slice of gel is destroyed by heating with 3 ml. of concentrated sulphuric acid in a pyrex tube, 100 vol. hydrogen peroxide being added in small amounts (1 to 2 drops) and boiled out after each addition, until destruction is complete; or the destruction may be, with advantage, finished with perchloric acid (60 per cent.), as in (*c*). The solution is then diluted to about 50 ml., and the chromate ion reduced by addition of a few drops of saturated sodium sulphite solution This reduction is necessary to avoid occlusion of chromate ion with the silver chloride in the next stage when the silver is precipitated by hydrochloric acid. The precipitate of silver chloride is separated by centrifuging and filtering, washed twice with dilute hydrochloric acid (1 in 10), and the filtrate and washings are evaporated to about 10 ml. This solution, with 3 ml. of concentrated sulphuric acid, is boiled down in a pyrex tube till fuming commences, when a few drops of 100 vol. hydrogen peroxide are added, and the liquid is again boiled to fuming, after which it is diluted to a suitable volume (50 or 100 ml.), and an aliquot part,

* The particular technique was evolved in these laboratories for the determination of chromium in chromatised ligatures.

representing not more than 0·05 mg. of potassium dichromate, is taken. This portion is diluted to 25 ml. and treated as follows:

A few drops of 0·1 *N* potassium permanganate solution are added, the liquid is brought to vigorous boiling, and more permanganate solution is added, drop by drop, until a permanent pink colour is obtained which is not destroyed by further boiling.

5 *N* sodium hydroxide solution is then added from a 10-ml. pipette until the solution is just alkaline (as indicated by a change of colour and formation of precipitate), and 5 ml. are added in excess. The solution is then boiled; if it does not then become green, more permanganate solution is added, drop by drop, during vigorous boiling, until the liquid is just permanently green. Care must be taken to avoid the addition of more permanganate than is necessary. The liquid is then cooled to room temperature, filtered through a sintered glass filter, which is washed with about 20 ml. of water, the total liquid, which should be green and quite clear, being collected in a 100-ml. Nessler tube (A).

A control solution, in another Nessler tube (B), is prepared by diluting 5 ml. of 5 *N* sodium hydroxide solution with 20 ml. of water, adding 1 drop of 0·1 *N* potassium permanganate solution and cooling to room temperature. The liquid in A is diluted to about 70 ml., and that in B to about 60 ml., and to each are added 20 ml. of 10 *N* sulphuric acid and 5 ml. of the diphenyl-carbazide reagent (0·1 per cent. in 25 per cent. acetic acid solution). The colour in A is then nearly matched in B by the addition of standard potassium dichromate solution (0·0005 per cent.); both liquids are then made up to the mark, and more standard potassium dichromate solution is added to B until the colours are exactly matched.

(*c*) *Silver* in small amount [too small for method (*a*), *e.g.* amount equal to 1 ml. of 0·001 *N* silver or less], with chromate ion in small amount, or in excess.

The method comprises separation of silver from the chromate ion by extraction with diphenyl-thiocarbazone (dithizone) and subsequent determination of the silver by Jelley's[6] colorimetric method.*

The slice of gel (about 5 g.) is put into a pyrex tube, and destruction is effected by heating after the addition of 1 ml. of concentrated sulphuric acid and 4 drops of 60 per cent. perchloric acid solution. The solution is then diluted to 50 ml. with water, 20 ml. of this being used for the determination of chromate ion and 20 ml. for silver.

Determination of Chromate Ion.—Method (*b*), previously described, is used.

Determination of Silver.—To the 20 ml. of solution one drop of saturated sodium sulphite solution is added to reduce chromate, 2 ml. of 50 per cent. citric acid solution are added, and the solution is made alkaline with 10 ml. of 5 *N* ammonia and washed into a separating funnel with about 10 ml. of water. This mixture is then extracted twice (or more often, if necessary, until the colour of the

* The reactions of diphenylthiocarbazone ("dithizone") were described by Fischer,[7] and its use for the determination of small amounts of lead was first suggested by Allport and Skrimshire[8] for the determination of lead in dyestuffs. Interest in the reagent was thereby stimulated, and it has since been the subject of considerable investigation, particularly by Fischer[9] and his co-workers. Nevertheless, the general utility of the reagent for the separation of metals preparatory to their determination does not yet appear to have been fully appreciated. It may be mentioned that a method has been developed in these laboratories for the determination of zinc in food materials by means of this reagent.

reagent remains unaltered) with 10 ml. of dithizone solution* (0·15 per cent. reagent in chloroform), and the bulked chloroform extract is twice washed with 20 ml. of water, placed in a pyrex tube (8 in. by 1 in.) and evaporated to dryness in a water-bath, the residue then being "destroyed" by heating with 1 ml. of concentrated sulphuric acid and 4 drops of 60 per cent. perchloric acid.

The resulting solution is transferred to a 50-ml. flask and diluted with water to about 20 ml., after which the procedure is according to Jelley's method from the stage of addition of bromine water.

Example.—0·2 g. of 5 per cent. gelatin containing 0·2 mg. of silver with 1 ml. of 0·1 *N* potassium chromate added.

Found: 0·202 mg. of silver.

(II) CALCIUM PHOSPHATE.—The method of Washburn and Shear[10] gave satisfactory results. The agar in the slice of gel (about 1 g.) does not interfere.

(III) MAGNESIUM CHLORIDE AND AMMONIA.—The magnesium, hydroxyl, ammonium, and chlorine were all determined from the same slice of gel (about 1 g.): first the OH by solution in acid and back-titration, then the NH_4, and the residue after distillation was made up to a definite volume and one portion taken for determination of magnesium and another for chlorine.

Handy's[11] method of titration of the magnesium ammonium phosphate was found useful when a large number of determinations had to be made.

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In conclusion I wish to express my thanks to Messrs. J. Lyons & Co., Ltd., for facilities to pursue this investigation.

* The reagent should be free from copper.

Determination of Physiological Activity of Hemp Resin by a Polarimetric Method

M. N. GHOSE, B.Sc. AND S. N. BHATTACHARJEE

THE physiological activity of the hemp drugs (obtained from *Cannabis sativa*, Linn.), *viz.* charas, ganja and bhang is associated with their resins, although the chemical nature of the active principle is still unsettled. Personne (*J. Pharm. Chim.*, iii, **31**, 46), by repeated distillation of the same portion of water from large quantities of hemp renewed at each distillation, obtained a volatile oil with a strong odour of hemp. He thought that this was the active principle of the plant and named it "cannabene." Kobert, in 1894, isolated from *Cannabis indica* a dark and oily liquid, which he called "cannabindone." Subsequently, Wood, Spivey and Easterfield (*J. Chem. Soc.*, 1896, **69**, 539), while investigating charas, isolated a resinous substance boiling at 265° to 270° C. under a pressure of 20 mm. To this product they gave the name "cannabinol" ($C_{18}H_{24}O_2$). They considered it to be the only active ingredient of hemp. Frankel, however (*Arch. Exp. Path. Pharm.*, 1903, 266), claimed to have isolated the active principle of hemp as a pure, chemically well-defined body—a phenol aldehyde having the formula $C_{21}H_{30}O_2$. He termed this product "cannabinol," and suggested the term "pseudo-cannabinol" for the substance isolated by Wood, Spivey and Easterfield.

It has been ascertained, however, that the resin-content of a hemp drug is not a measure of its potency. Hemp resin is a complex substance, and attempts to isolate the active principle from it have not yet been successful. This is probably because the active principle is unstable and undergoes rapid oxidation. Hooper (*Pharm. J.*, 1908) evolved a chemical method for evaluating Indian hemp. He based his results on the iodine values of the dried alcoholic extracts of the drugs. Subsequently, however, the results of experiments in this laboratory proved that this is not always valid. Marshall and Wigner (*Pharm. J.*, 1911, **86**, 739) also showed that there was no definite relationship between the iodine value and the physiological activity of different samples. Marshall and Wood (*Brit. Med. J.*, 1912, 2234) examined the acetylation method, and found that also to be of little value. The general opinion is that the only reliable method for determining the physiological activity of hemp drugs is to study their physiological action on animals, especially dogs, but animal tests are not always trustworthy, for the animal itself becomes immune by repeated administration of the drug.

Sudborough and Rao, in "Tests for Ganja and other Products of Indian Hemp" (1918), have described certain qualitative tests for hemp resin, but, since ganja several years old will respond to these tests, that they have no definite relation to the amount of active principle.

We have attempted to formulate a suitable method for determining the physiological activity of hemp drugs. It has been known for some time in this laboratory that charas and resin extracted from ganja are also optically active. A polarimetric method has been devised for the assay of the drug. As a result of experiments on a large number of resins extracted from samples of charas (the

resinous substance that appears spontaneously on leaves, stems, inflorescences and fruits of the hemp plant *Cannabis sativa*, Linn.), it has been found that the specific rotation of the resin of good and fresh charas is about −105°, whilst that of older and inferior material is as low as −64°. Samples with specific rotation −95° have about seven-eighths of the normal potency, those with rotation −85° to −92° about three-quarters, and those with rotation −77° to −80° about five-eighths, and so on. The specific rotation for exceptionally potent charas has been found to be about −115°, but such samples are rare. The method for the determination of specific rotation is as follows:

Two grms. of the sample are boiled in a Soxhlet tube under a reflux condenser for about 4 hours with about 75 ml. of carbon tetrachloride. The carbon tetrachloride extract is shaken with about 10 grms. of fused calcium chloride, and is

Resin Per Cent.	Ash Per Cent.	Other vegetable matter and moisture (by diff.) Per Cent.	"Specific rotation" $[\alpha]_D$	Opinion of experienced smokers
37·7	38·2	24·1	−114·8°	normal
35·6	36·5	26·9	−113·6°	normal
34·7	35·9	29·4	−109·8°	normal
32·6	37·2	30·2	−106·3°	normal
38·9	34·8	26·3	−106·0°	normal
36·7	38·5	24·8	−104·8°	normal
36·3	32·0	31·7	−104·3°	normal
37·6	37·2	25·2	−104·0°	normal
33·3	31·0	25·7	− 95·7°	7/8th normal
32·7	36·5	30·8	− 92·6°	3/4th normal
30·0	40·5	29·5	− 92·4°	3/4th normal
41·5	37·1	21·4	− 91·8°	3/4th normal
34·5	34·2	31·3	− 90·4°	3/4th normal
38·4	30·5	31·1	− 90·2°	3/4th normal
38·0	40·2	23·8	− 86·6°	3/4th normal
30·8	38·6	31·4	− 86·6°	3/4th normal
34·2	27·0	38·8	− 85·0°	3/4th normal
33·2	41·6	25·2	− 77·2°	5/8th normal
25·2	40·3	34·5	− 68·8°	5/8th normal
32·5	35·7	31·8	− 64·0°	1/2 normal

immediately filtered and made up to 100 ml. The rotation of the extract is determined at the room temperature in a decimeter tube. The percentage of resin in the drug is calculated by evaporating 50 ml. of the extract in a platinum dish and weighing the residue to constant weight at a temperature not above 90° C. The specific rotation of the resin of the drug is calculated by the following formula:

$$[\alpha]_D = \frac{100 \times 0{\cdot}3465 \times X^\circ}{C}$$

where $[\alpha]_D$ is the apparent specific rotatory power of the substance,

X the reading on the Schmidt and Haensch (Ventzke) sugar scale, and

C the concentration of the solution in grms. per 100 ml.

In the absence of a more suitable standard of measurement, the degree of intoxication which a smoker experiences under ordinary circumstances has been

taken as the measure of potency of the drug. The standard coin in India is the rupee, divisible into sixteen annas; hence the smokers usually mention the strength of the intoxicants in terms of annas, or more frequently in couples of annas. Thus, according to them, full strength is sixteen annas, 5/8th strength is 10 annas, and so forth.

Four habitual smokers, unknown to one another, and aged 60, 45, 37, and 32, were supplied with the same sample to smoke at their usual hours. The next day their opinions were taken. They usually agreed with one another, and differences of more than one anna were rare. We have not taken into account their estimate to 1/16th unit.

The results obtained with a number of charas (hemp resin) samples are tabulated on p. 314.

Making allowances for the variability of opinion of even experienced smokers, it will be seen that the more active the resin the higher is its specific rotation.

The resin of ganja (the flowering tops of the female hemp plant which, like charas, are smoked in India for intoxication) was extracted with carbon tetrachloride, and its specific rotation was determined in 4 per cent. solution. The results of some experiments are tabulated below:

Resin Per Cent.	Ash Per Cent.	Other vegetable matter and moisture (by diff.) Per Cent.	"Specific rotation" $[\alpha]_D$	Opinion of experienced smokers
13·1	15·7	71·2	−95·2°	normal
15·5	14·0	70·5	−94·1°	normal
13·3	13·4	73·3	−93·6°	normal
13·8	16·2	70·0	−90·4°	normal
14·3	13·8	71·9	−90·2°	normal
15·5	14·7	69·8	−89·4°	normal
11·7	15·0	73·3	−80·0°	7/8th normal
15·0	13·5	71·5	−77·0°	7/8th normal
12·8	14·6	72·6	−75·1°	3/4th normal
8·4	16·2	75·4	−74·3°	3/4th normal
15·0	16·1	68·9	−69·8°	5/8th normal
11·6	16·1	74·6	−67·2°	5/8th normal
13·5	16·6	69·9	−60·0°	1/2 normal
13·0	17·5	69·5	nil	almost nil

The specific rotation of ganja of good quality may be taken as about −90°, and that of inferior quality as −60° or less. Samples with rotations of −77° to −80° are about 7/8th active; with rotation −75° about 3/4th; with rotation −67° to −70° 5/8th active, and so on. The rotation of very old samples, having the usual resin-content but very little physiological activity, is practically nil (*vide* the last sample above). It may be mentioned, in passing, that chlorophyll, which is usually present in appreciable amount in ganja of poor quality, interferes with the transmission of light through the polarimeter.

It thus appears that in both charas and ganja there is some definite relationship between the specific rotation of the drug and its physiological activity.

This investigation has been carried out at the Chemical Laboratory, Calcutta Custom House, and is published by permission of the Collector of Customs, Calcutta. We are also indebted to the Special Chemical Adviser, Central Board of Revenue, Government of India, for his interest in this paper.

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Notes

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

THE DIRECT TITRATION OF SOLUBLE ORTHOPHOSPHATES WITH LEAD ACETATE IN THE PRESENCE OF DIBROMOFLUORESCEIN AS ADSORPTION INDICATOR

IN a previous communication (ANALYST, 1933, **58**, 331) I described titration methods, with lead acetate as the precipitant, for the determination of caustic alkalis and borates in the presence of a suitable adsorption indicator. I have also used lead acetate as the precipitant in the titration of oxalates (*Trans. Faraday Soc.*, 1932, **28**, 561, 565).

The method can also be applied to the direct titration of orthophosphates, in neutral or weakly acid solution, in the presence of dibromofluorescein as the adsorption indicator. The best results are obtained with 0·05 molar concentrations of phosphate and lead acetate, though accurate results may be obtained with 0·005 molar solutions. A 0·1 per cent. alcoholic solution of the indicator is employed.

The reactions involved in the titration processes can be represented by the equations:

(1) $2NaH_2PO_4 + 3(CH_3COO)_2Pb = \downarrow Pb_3(PO_4)_2 + 4CH_3COOH + 2CH_3COONa.$

(2) $2Na_2HPO_4 + 3(CH_3COO)_2Pb = \downarrow Pb_3(PO_4)_2 + 2CH_3COOH + 4CH_3COONa.$

(3) $2Na_3PO_4 + 3(CH_3COO)_2Pb = \downarrow Pb_3(PO_4)_2 + 6CH_3COONa.$

The acetic acid liberated in the first two titrations is too weak an acid to affect the accuracy of the determinations. The presence of mineral acids, however, must be avoided, owing to their solvent action on the precipitated lead phosphate. With an orthophosphate, such as Na_3PO_4 (which is strongly alkaline) or Na_2HPO_4 (which is slightly alkaline), the solution must first be neutralised with nitric acid; with NaH_2PO_4 (which is slightly acid) neutralisation is not necessary. The following account of the titration of disodium hydrogen phosphate explains the method:

The Titration of Disodium Hydrogen Phosphate.—Twenty-five ml. of 0·05 *M* disodium hydrogen phosphate solution are neutralised with 0·01 *N* nitric acid, with phenolphthalein as indicator, 3 or 4 drops of a 0·1 per cent. alcoholic solution of the adsorption indicator are added, and the mixture is titrated with 0·05 *M* lead

acetate solution; the addition of the indicator imparts an orange colour and fluorescence to the solution. The titration is continued, with vigorous shaking, until a permanent pink colour is observed on the precipitate of lead orthophosphate.

If 0·005 *M* solutions of phosphate are employed, 1 to 2 drops of the indicator must be added to 25 ml. of the phosphate solution. It is very important not to add excess of indicator; in order to give a sharp end-point, a high proportion of the dyestuff present in the solution must be adsorbed on the precipitate at the end-point. As the orange fluorescence of the original solution has a pale red reflex, an excess of the indicator would render the true end-point rather uncertain.

The mechanism of the titration is as follows:

1. As the titration proceeds, the excess of $PO^{\equiv}$ ions is adsorbed on the surface of the precipitate of lead orthophosphate, to form the complex body $[Pb_3(PO_4)_2]PO_4^{\equiv}$*

2. In the presence of a slight excess of Pb^{++} ions, the phosphate ions are displaced by Pb^{++} ions from the surface of the equivalent-body (*i.e.* the precipitate at the exact equivalent-point). The equivalent-body now becomes $[Pb_3(PO_4)_2]Pb^{++}$.*

3. This positively charged body repels the remaining free Pb^{++} ions, but attracts the negatively charged anions of the indicator; and, as a result of this deformation of the electron systems of the latter, the colour and tendency to fluoresce of the dyestuff anions are altered. The accompanying colour change renders the adsorption visible at the equivalent-point, and an accurate titration becomes possible.

Since the titration can be carried out in weak acid solution, it is possible to titrate phosphoric acid in this manner, although this would seldom be necessary, as accurate alkalimetric titrations are available. The titration is correct to 0·5 per cent.

An interesting fact was noticed in attempting to titrate a solution of metaphosphoric acid by this method: it was found that the amount of lead acetate required was three times the theoretical amount calculated for the formula HPO_3. It is a well-known fact that, in addition to simple metaphosphates, metaphosphates derived from polymeric acids, $(HPO_3)_n$, are known, where n may be 1, 2, 3, 4, or 6. It seems likely, therefore, on the basis of this experiment, that lead metaphosphate is derived from the polymeric acid $(HPO_3)_3$. (Cf. *Inorganic Chemistry*, T. M. Lowry, p. 432.)

The experimental results of a number of titrations are given below. The method of procedure was to prepare an accurate 0·05 molar solution of the phosphate by weighing the required amount of the purest analytical reagent and dissolving it in CO_2-free water. In preparing these solutions the hydrated salt was used in most cases, but, for convenience in comparison, the weights given in the table are expressed in g. per l. of the anhydrous salt. The 0·05 molar solution of lead acetate was standardised with 0·01 *N* NaOH (ANALYST, *loc. cit.*). It will be seen

* It has been shown by Lottermoser (*J. prakt. Chem.*, 1905, **72**, 39; 1906, **73**, 374) that a precipitate which has been formed by the combination of oppositely charged ions, exhibits an electrical charge with respect to its saturated solution; the sign of the charge depends on the ion which is present in excess in solution. For example, in the presence of an excess of Cl^- ions a precipitate of AgCl exhibits a negative charge with respect to the solution, and a positive charge when Ag^+ ions are present in excess. This can only mean that these ions are adsorbed on the surface of the ion-lattice of the precipitate, and the complex bodies thus formed can be represented quite arbitrarily by the formulae $[AgCl]Cl^-$ and $[AgCl]Ag^+$. Consequently, in the presence of an acidic adsorption indicator, such as a fluorescein derivative, the negatively charged anions of the dyestuff are attracted to the surface of the precipitate when it is positively charged, *i.e.* when Ag^+ ions are present in excess; the characteristic colour of the indicator anion is thereby altered. This fact, among others, has been used by Prof. Fajans as the basis of his Theory of Adsorption Indicators.

In the formulae of the complex bodies occurring in the phosphate titration given above it should be realised that they do not represent definite compounds, but serve as a conventional representation of the states of the *surface* of the precipitate during the titration.

that the results are quantitative within an error of 0·2 per cent. Similar accurate results were obtained with 0·01 molar solutions.

Phosphate	No. of ml. of 0·05*M* lead acetate required by 25 ml. of phosphate solution	Concentration of anhydrous phosphate in g. per l. determined	
		(*a*) By titration	(*b*) By weighing
NaH_2PO_4	37·5	6·00	6·00
Na_2HPO_4	37·4	7·08	7·10
Na_3PO_4	37·4	8·18	8·20
KH_2PO_4	37·5	6·81	6·81
K_2HPO_4	37·4	8·69	8·71
K_3PO_4	37·4	10·59	10·61
$NaNH_4HPO_4$	37·3	6·82	6·85
$(NH_4)_2HPO_4$	37·4	6·58	6·60

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A NEW REAGENT FOR ELIMINATING THE INTERFERENCE DUE TO CALCIUM IN THE VOLUMETRIC FEHLING'S TITRATION FOR INVERT SUGAR

EYNON and Lane (*J. Soc. Chem. Ind.*, 1923, **42**, 143T) have shown that the presence of the alkaline earth metals, more particularly calcium, decreases the copper-reducing power of sugar solutions. They suggested precipitation with potassium oxalate to remove the calcium, and demonstrated that this was a satisfactory procedure.

In a recent number of the *Chemical Trade Journal* (November 16th, 1934, p. 358) some details are given of the production and use of sodium hexametaphosphate (Calgon) for water-conditioning. It has been suggested that Calgon ionises to two sodium ions and a complex of the formula $Na_4P_6O_{18}$, and that calcium can be substituted for sodium in this, giving $CaNa_2P_6O_{18}$, which is soluble. When an excess of Calgon is added to a calcium solution the calcium becomes inert and cannot be detected by any of the normal reagents.

Provided that Calgon would retain its identity in the presence of Fehling's solution, its use might allow of the determination of invert sugar in solutions of invert sugar containing calcium. A preliminary test confirmed this. Further, there was no lag in the end-point, as is the case when calcium is present. Accordingly, the following experiments were made:

A 0·5 per cent. solution of pure invert sugar was used to standardise the Fehling's solution under standard conditions, methylene blue being used as indicator. Varying quantities of Calgon were then added to the Fehling's solution immediately before the addition of invert solutions, obtained from pure sugar and molasses which were known to contain insufficient calcium to affect the titration. In no case did the presence of the Calgon affect the result.

Calgon added	Titration Ml.	Theory Ml.
40 ml. of a 1 per cent. solution	20·00	20·00
30 ml. of a 5 ,, ,, ,,	24·70	24·70
20 ml. of a 10 ,, ,, ,,	24·70	24·70
10 ml. of a 33 ,, ,, ,,	26·55	26·50

Sufficient *N* calcium chloride solution was then added to solutions of sugar and molasses to give a *N*/100 concentration of calcium in the titrating solution. Titrations were made, with and without the addition of Calgon. As only a small amount of calcium can enter the Calgon complex, an excess of the reagent (10 ml.

of a 33 per cent. solution) was used. In all cases interference due to the calcium was eliminated.

Finally, a series of molasses was obtained, all of which were known to contain calcium. Titrations with solutions of these were carried out in triplicate.

(i) Without removal of the calcium.
(ii) With removal of the calcium by potassium oxalate.
(iii) Without removal of the calcium, but with the addition of 10 ml. of a 33 per cent. solution of Calgon.

In the following table the figures in the second, third and fourth columns represent ml. of the inverted solution of the molasses:

Sweetening matter content of molasses Per Cent.	Titration (i) Ml.	Titration (ii) (oxalate separation) Ml.	Titration (iii) Ml.
75	26·70	26·50	26·55
70	28·90	28·30	28·35
	28·90	28·25	28·40
70	29·05	28·35	28·35
	28·95	28·15	28·25
50	38·50	37·70	37·65
	38·60	37·70	37·70
50	41·15	40·10	40·10
	41·25		40·10

From these results it is clear that the addition of 10 ml. of a 33 per cent. solution of Calgon to the Fehling's solution immediately before the addition of the invert sugar solution will satisfactorily eliminate any interference due to the presence of calcium.

I have to thank the Government Chemist, Sir Robert Robertson, K.B.E., F.R.S., for permission to publish this note.

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CHARACTERISTICS OF SANDALWOOD SEEDS AND SEED OIL (MYSORE)

ALTHOUGH there is an extensive literature on sandalwood (*Santalum album*), nothing has been published about the seeds, except by Watt (*Dictionary of the Economic Products of India*, Vol. VI, Part II), who mentions that they contain a fatty oil which is used by the natives for burning purposes.

Santalum album (N.O. *Santalaceae*) is an evergreen tree, which grows wild in certain parts of the Mysore State, Coorg, Coimbatore, and the southern parts of Madras. It grows at different altitudes from the sea level to about 4000 feet, and the trees in the forests vary in height from 12 to 35 feet. The total area of sandalwood plantations in Mysore and Coorg has been roughly estimated to amount to 5200 square miles. The tree bears fruit twice a year, and the dried seeds are of the size of a large pea. The seed kernels, which are edible, are rich in oil, and, as the pericarp is fairly soft, the kernel can be easily separated by hand. A plentiful supply of the seeds could be obtained during the seasons if proper measures for their collection were enforced. At present, however, they are left to rot under the trees, only a small quantity being collected and exposed for sale in the bazaars by a few druggists.

In view of the lack of analytical data concerning the seed oil, four samples of seed obtained from different localities in Mysore, and two from Kuppam in Madras,

have been examined. In each case 1 kg. of the seed was crushed in a mortar, and the meal was extracted with petroleum spirit for 14 hours in Soxhlet extractors. From 44 to 49 per cent. of oil, ranging in colour from golden yellow to dark reddish-brown (according to the colour of the pericarp), was obtained.

The oil absorbs about 15 per cent. of its weight of oxygen from the air in 4 days, passing through an intermediate tacky stage and finally forming a thin, elastic skin. At higher temperatures the oil thickens, becoming very viscous, and ultimately gelatinises in a short period. When heated in the presence of driers for 64 hours in a thin film it yields a glossy unbroken film. The oil can be readily bleached by treatment with sulphuric acid and dichromate.

The unsaponifiable matter is a highly unsaturated resinous substance (Wijs iodine value about 300).

The results tabulated below were obtained by the methods suggested by Bolton in the latest edition of *Oils, Fats and Fatty Foods*.

	Locality					
	Heggada			Bangalore	Kuppam	
	Sagar	Devanakote	Kolar	bazaar	A	B
Wt. of 100 seeds, g.	13·6	14·2	13·4	12·7	15·0	14·6
Wt. of 100 seeds without pericarp, g. ..	6·6	6·8	6·0	5·7	7·3	6·9
Oil-content of seed, per cent.	47	48·5	46·4	43·9	49	48·5
Refractive index, n_D^{60}	1·4780	1·4760	1·4765	1·4770	1·4770	1·4780
Sp.gr. of oil at 25° C.	0·938	0·936	0·928	0·930	0·945	0·940
Saponification value	190	188	185	191	194	197
Iodine value (Wijs)	145	149	142	138	153	146
Acetyl value	23	23·5	21·8	20·4	22·9	24·3
Acid value (as oleic acid), per cent. ..	11	11·7	10·5	13·6	14·5	14·1
Unsaponifiable matter, per cent. ..	17·5	18·2	16·8	17·1	18·8	18·1
Nitrogen-content of seeds, per cent. ..	1·98	1·93	1·84	1·76	2·1	1·97
Nitrogen-content of exhausted seeds, per cent.	3·73	3·78	3·69	3·41	3·8	3·76

The mixed fatty acids had: Molecular equivalent, 285; iodine value (Wijs), 102; solidification pt. (titre test), 35° C. The "solid" fatty acids (40 per cent. of the total acids) had: Molecular equivalent, 278; iodine value, 10·5.

Promising results have been obtained in experiments on the use of the crushed seed (as a substitute for linseed) for a poultice material, and with the unsaponifiable matter as a vehicle for ointments. In two experimental trials, $\frac{1}{4}$ lb. of the soaked and crushed meal was given to cows with their usual fodder. They ate it readily and showed no indications of illness after 10 days.

I wish to thank Professor T. P. Hilditch for his advice and for suggesting a scheme for the further investigation of this oil.

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SHREDDED SUET: A NEW MATERIAL USED FOR COATING

In January last an informal sample of shredded suet was submitted to us. It was of very good appearance, the shreds evenly coated, fairly easily detachable from one another, and the packet contained no detached coating material.

The legend on the packet read as follows:—"Refined and coated with a specially prepared flour. Guaranteed free from preservative, colouring matter, rice or other starches, and to conform with the Food and Drugs Act. It is sold as a mixture consisting of Pure Refined Beef Suet enriched by the addition of about 12 per cent. of a pure food product introducing valuable proteins, carbohydrates and vitamins."

This led us to suspect soya bean meal, and we confirmed this by the microscope. We found the sample to be composed of

Soya bean meal ..	6·5
Fat	91·5
Water, etc.	2·0
	100·0

We passed the sample as genuine.

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THE CORROSION OF LEAD IN BUILDINGS*

THE causes of the various types of corrosion of lead that may occur in connection with building materials may nearly all be classified as due to contact with cement, timber or soil, but reference must also be made to the effect of elastic fatigue of the metal in accelerating its decay.

I. CORROSION CAUSED BY CEMENTS AND MORTAR.—Superficial injury of lead damp courses in contact with mortar is relatively common, the lead becoming coated with patches of red powder, but complete destruction is rarer. Instances are also recorded in which lead pipes imbedded in soil have been partly converted into a mass of red and yellow lead oxide in alternating rings, which, according to Kohlmeyer (*Chem.-Ztg.*, 1912, **36**, 993) are periodic in character, the red rings (consisting of Pb_3O_4) representing the dry season of the year, and the yellow rings of PbO representing the wet season.

The general opinion of builders and plumbers is that cement is much more corrosive than mortar. This is supported by cases investigated at the Research Station, and is to be attributed to the more rapid carbonation of lime mortar than of cement mortar.

In past investigations into the causes of corrosion by lime and mortar it has been shown that calcium bicarbonate has no action, owing to the formation of a protective film. Slaked lime was found to cause rapid corrosion, whilst carbonated lime mortar afforded protection against solution of the lead.

A solution containing calcium carbonate, calcium sulphate, and 0·8 g. of calcium [as $Ca(OH)_2$] per litre, *i.e.* nearly saturated, caused rapid attack; hence the corrosive action of lime solution is not prevented by the presence of gypsum and chalk.

Heyn's observation (*Deutscher Ausschuss für Eisenbeton*, 1911, Heft 8), that gypsum protects lead from corrosion by water, but not from attack by lime solution, has been confirmed.

In experiments in which cleansed lead sheets were three parts immersed in various solutions and suspensions and subjected for a month to the action of a

* Technical Paper, No. 8. By F. L. Brady, M.Sc., A.I.C. Revised edition, pp. 25. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1934. Price 1s. 1d., post free.

current of air free from carbon dioxide, the following comparative amounts of lead were found in the filtered liquids:

	Weight of lead per 100 ml. g.
Distilled water	0·009
Saturated lime water	0·108
Portland cement suspension	0·183
High alumina cement suspension	0·012
Portland blast-furnace cement suspension	0·162

So long as the specimen is losing weight regularly and no surface deposits are being formed, the change of apparent weight in water can be used to calculate the rate of removal of lead, *i.e.* the rate of oxidation. The following rates of oxidation were calculated from results in which the air was bubbled through the solution at a controlled rate:

	Rate of oxidation per sq.cm. per hour Mg.
Distilled water	0·28
High alumina cement	0·10
Saturated lime water	0·42
Portland cement	0·46
Saturated lime water, specimen not cleaned, covered with oxidation film	0·53
Saturated lime water, specimen previously tested 3 days in tap water	0·31

The lower rate of corrosion in a suspension of high alumina cement, as compared with Portland cement suspension, was to be expected in view of the fact that the alumina cement contained no free lime.

When exposed freely to atmospheric weathering, or when immersed in water containing calcium bicarbonate, lead rapidly develops a protective film of corrosion product. The film does not, however, afford any useful degree of protection against contact with lime or cement.

Nature of the Products of the Interaction of Oxygen and Lead in presence of Lime Solution.—Attempts to obtain a solid compound of lime with lead oxide, a calcium plumbite, have failed, since the solution decomposes on evaporation. Solutions obtained in a series of tests were examined by ultra-filtration, and the ratios of CaO to Pb of the solutions, before and after filtration, were essentially the same. These results indicate that a true solution of lead oxide in lime solution is formed, and strongly suggest the formation of a chemical compound which is a calcium plumbite. A small proportion of the lead present appears to be in colloidal solution.

METHODS OF PREVENTION.—Coating the lead with bitumen or, better, with bitumen-impregnated felt, affords good protection. Lime mortar exposed to the air carbonates more rapidly than cement mortar, and is therefore to be preferred to Portland cement for bedding lead damp-courses, pipes or electrical conduits. Additions to cement mortar do not offer much prospect of usefulness. No pronounced beneficial result has been observed by incorporating sodium silicate with cement. Tests amply confirm the opinion as to the comparative harmlessness of high alumina cement. The replacement of pure lead by alloys containing small proportions of tin, antimony and cadmium deserves attention (see Building Research Special Report, No. 19).

The extent of protection afforded to "Compo" pipes must depend upon the thickness and continuity of the tin coating. In one case examined the coating was too thin to make the lead resistant to corrosion by cement.

II. CORROSION CAUSED BY TIMBER.—Serious corrosion is frequently caused where lead is used in contact with timber. The typical case of such contact is where sheet lead is laid over oak boarding. The attack of lead by oak is analogous to the Dutch process for the manufacture of white lead. The minute quantities of organic acids in the wood are sufficient to cause slow but progressive corrosion during a period of years. In this connection the possibility of corrosion of lead by acetic fumes from manufacturing processes should not be overlooked. Injury to the lead covering of glazing bars in the roof of a pickle factory was found to be due to this cause. The lead had softened and a deposit of white powder (identified as white lead) was present on the benches and the floor.

The following conclusions were drawn from the various cases investigated:

(i) With oak that is fairly well seasoned, corrosion is not appreciable in two months, provided that access of water is prevented.

(ii) Under moist conditions seasoned oak rapidly corrodes lead. As a preventive, bitumen felt is effective, but a bitumen paint may not afford protection.

(iii) Soft woods may cause appreciable corrosion of lead, but to a much less extent than oak.

(iv) The only hardwood tested—teak—behaved similarly to oak.

III. CORROSION CAUSED BY SOIL.—Most soils are innocuous, but it cannot be assumed that, under natural conditions, combinations may not arise that will cause corrosion to occur with any type of soil—clayey, peaty or sandy. The decay of lead in soil usually leads to the formation of a white deposit of basic lead carbonate, sometimes containing lead chloride or traces of other lead compounds. Analysis of deposits examined by Leybold (*Dingl. polyt. J.*, 1887, **266**, 220) suggests that in those instances the corrosion was due to causes similar to those operating in the decay of lead by timber, and that the decay was due to dilute organic acids acting in the presence of moisture, oxygen and carbon dioxide.

Failures of lead pipe in made-up ground are known. Such ground may contain coal ashes with soluble salts, and also decaying vegetable refuse, so that different types of corrosion are possible.

To prevent possible troubles, the pipes may be laid in some corrosion-inhibiting substance, such as chalk, limestone or old, well-carbonated lime-mortar, or the pipes may be wrapped with felt strips impregnated with bitumen. The substitution for lead of suitable lead alloys will also prevent trouble.

International Vitamin Standards

WE are asked to announce that the International Standards for vitamins *A*, B_1, *C*, and *D* are now available for issue to laboratories, institutions and research workers in Great Britain and Northern Ireland. These standards were accepted for international use at the Second International Conference on Vitamin Standardisation held in London in June, 1934, under the auspices of the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations.

The Conference recommended that they should be kept at the National Institute for Medical Research, Hampstead, N.W.3, which would act for this purpose as central laboratory on behalf of the Health Organisation of the League of Nations. The required quantities of each of the Vitamin Standards are now being sent to national central laboratories for subsequent local distribution in countries abroad.

The National Institute for Medical Research, London, will continue to supply the International Vitamin Standards for use in Great Britain and Northern Ireland. The standards for the Vitamins B_1 and D remain unchanged, and their supply at regular half-yearly intervals will be continued as before. The standard for Vitamin A has been changed, a pure specimen of β-carotene having been adopted in place of the impure preparation of carotene hitherto employed. The unit of Vitamin A remains unchanged, though it is now defined as the Vitamin A activity contained in 0·6 microgram of pure β-carotene. In accordance with the recommendations of the Conference, the β-carotene is issued in the form of a solution in oil, of which 1 gram contains 500 International Units. The quantity of this standard solution supplied to each applicant is approximately 5 grams, and, on account of the small quantity available, it can be supplied only at yearly intervals, and not half-yearly as formerly. It is suggested, therefore, that care and economy should be exercised in its use, and that subsidiary laboratory standards, exactly assayed in terms of the International Standard, should be prepared for routine work.

l-Ascorbic acid has been adopted as the International Standard for Vitamin *C*, the unit of activity being defined as the vitamin *C* activity contained in 0·5 milligram of pure *l*-ascorbic acid. A quantity of approximately 550 milligrams will be supplied to all laboratories, institutions and research workers in Great Britain and Northern Ireland, who require it.

It is requested that those laboratories, institutions and research workers in Great Britain and Northern Ireland who do not receive the standards at present, and who desire to receive any or all of them, will apply to the Director of the Department of Biological Standards, The National Institute for Medical Research, Hampstead, London, N.W.3.

Argentine Republic

DECREES OF THE MINISTRY OF LOCAL GOVERNMENT*

TOMATO CONSERVES

THE following Decree (No. 51,226, November 7, 1934) has been signed by the President of the Argentine Republic.

1. The name "Tomato Extract" shall be used to distinguish the conserve, obtained by concentration and sterilisation, containing not less than 16 per cent. of dry extract, free from sodium chloride.

2. "Single Extract of Tomatoes" shall contain from 16 per cent. to 28 per cent.; "Double Extract of Tomatoes," from 28 to 36 per cent.; and "Triple Extract of Tomatoes," not less than 36 per cent. of dry extract, free from sodium chloride. "Tomato Sauce" shall contain up to 16 per cent., and not less than 10 per cent. of dry extract, free from sodium chloride. No tomato conserve shall contain more than 5 per cent. of sodium chloride.

3. The proportions of dry extract specified in Section 2 shall be determined on homogeneous fractions of 2 to 3 g., which shall be submitted to continuous desiccation for exactly three hours in weighed glass crystallising vessels, with perfectly flat bottoms, and of the official pattern (diameter, 6 to 6·5 cm.; height, 1·8 to 2 cm.; thickness of walls, 1 to 1·5 mm.). The sample must be spread over the bottom of the vessel by means of a flexible spatula, so that the thickness of the layer shall not exceed 1 mm. From the total dry extract, calculated on 100 g. of the original sample, the amount of any sodium chloride present (determined by the usual methods) shall be deducted. A supplementary examination for substances extraneous to tomato pulp (adulterants, colouring matters, preservatives) shall be made.

4. Raw tomato conserve, obtained by pulping in the cold, shall be termed "Tomato Paste." It shall not contain more than 15 per cent. of sodium chloride.

* Leyes, Decretos y Resoluciones, 2nd Series, 1934. Ministerio de Hacienda, Buenos Aires.

5. The Department of Commerce and Industry shall require the foregoing descriptive names to be printed in prominent, easily legible type on the labels of the containers.

6. Manufacturers of sauces and extracts shall send out their products only in tin containers lined with sanitary lacquer, labelled with the correct descriptions, hermetically sealed by soldering after sterilisation, and containing not more than 20 kg. net weight.

Tomato pastes may also be sent out in wooden casks, not containing more than 20 kg. net.

The use of containers made of other adequate materials may also be authorised, subject to the approval of the Department of Commerce and Industry.

PERMISSIBLE AMOUNTS OF SULPHUR DIOXIDE IN WINES

By Decree No. 40,904 the amounts of sulphur dioxide that may be added to wine are regulated as follows:

It is prohibited to send out, or expose for sale, wines containing more than 320 mg. of total sulphur dioxide, with an allowance of 10 per cent. to compensate for errors in adding the preservative on an industrial scale.

Wines classified as "Sauterne" or "Sauterne Type," by the National Chemical Board (Oficinas Quimicas Nacionales) are allowed to contain up to 450 mg. of total sulphur dioxide.*

* Presumably, per litre, but the amount of wine is not mentioned in the Decree.—EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Is the Amylase Test alone sufficient to indicate Permanent Pasteurisation? M. F. Bengen and E. Bohm. (*Z. Unters. Lebensm.*, 1935, **69**, 146–152.)—With milk which has been heated for 30 minutes to 55° C., the ammonium sulphate serum always fails to give a positive test for amylase (*cf.* Rothenfusser, ANALYST, 1930, **55**, 758; Kluge, ANALYST, 1933, **58**, 168), a violet colour being obtained. Heating of milk at 50° C., even for 2 hours, does not, however, destroy the amylase completely, a yellow colour being invariably obtained. Comparative measurements have been made of the times necessary for the sera of milks subjected to various heat-treatments to degrade the starch used in the amylase test. The temperatures and times of heating (and the colours observed) were as follows: Raw milk, not heated, 3·5 hours (yellow); 50° C. for 30 minutes, 3·5 hours (yellow); 50° C. for 60 minutes, 4·5 hours (yellow); 50° C. for 120 minutes, 5·5 hours (yellow); 55° C. for 15 minutes, 10 hours (reddish-brown); 55° C. for 30 minutes, over 20 hours (violet); 60° C. for 15 minutes, over 20 hours (violet); 65° C. for 5 minutes, over 20 hours (violet). From these results, in conjunction with those previously obtained, it is concluded that the amylase test alone is inadequate to indicate if a milk has been heated for a sufficient time to ensure "permanent" pasteurisation. Failure to find amylase by the test shows only that the milk has been heated to at least 55° C. When used together with the turbidity test (*cf.* Bengen, ANALYST, 1933, **58**, 699) and the creamometric test (*cf.* Orla-Jensen, ANALYST, 1932, **57**, 383), the amylase test is able to show if any departure from the procedure laid down for permanent pasteurisation has been in the direction of insufficient heating or in that of addition of raw milk. Failure to answer to the amylase test, coupled with

response to the turbidity and creamometric tests, indicates milk which has been insufficiently heated at a temperature above 55° C. but below 63° C. On the other hand, response to all three tests indicates raw milk, either alone or mixed with heated milk.

For fresh milks the *p*H values lie between 6·8 and 6·75, and for pathologically altered milks values ranging from above 6·8 to 7·3 have been found; the values for the ammonium sulphate limiting serums agree to within about ±0·1 with those for the original milks. When applied directly to milks having *p*H values below 5·9 (degrees of acidity above 13), the amylase test either fails or gives indefinite results; if milk shows more than 10 degrees of acidity, this should be brought down to 6 or 7 before its behaviour towards the amylase test is examined. This test is applicable also to butter-milk. Addition of 10 per cent. of goat's milk to cow's milk renders the ammonium sulphate limiting serum turbid, and when more than 30 per cent. is added, the filtration is slowed down almost to stopping-point. T. H. P.

Microscopy of the Husks of the Principal Cereals. H. Härdtl. (*Z. Unters. Lebensm.*, 1935, **69**, 113–127.)—When cereal flours are boiled with dilute alkali hydroxide solution and the residue is washed with water, microscopic examination reveals the presence of fragments of transparent tissue, which do not appear to correspond with any described hitherto. These fragments are incapable of swelling and possess no structure resembling cellular structure. They are not lignified and are hence extremely pliable, so that they can assume the most varied shapes. A high magnification is often necessary for their identification. Descriptions and drawings are given of pieces of such tissue found in wheat bran, rye-meal and bran, barley-meal and bran, oat-meal and bran, and maize meal. The husks of cereals sometimes show lignified tissues. With wheat and rye, the extent of such lignification varies with the degree of ripeness of the corns. Unlike rye of good quality, shrivelled grains show no lignification, either in the intact grains or in the ground condition; a means of distinguishing between ryes of good and poor quality is thus furnished. The chemical nature of the cell-walls of the various tissues of the above cereals has been investigated microchemically with alkali hydroxide, zinc chloride and iodine, sulphuric acid, and phloroglucinol and hydrochloric acid. T. H. P.

Maize in South Africa. B. Segal. (*J. Chem. Met. Mining Soc. S. Africa*, **1934**, **35**, 163–169.)—Maize is grown in the Union of South Africa in approximately the proportions of 66 per cent. of dent maize, 33 per cent. of flint maize, and 1 per cent. of *Zea mays everta* (pop corns), *saccharata* (sweet corns), *amylacea* (soft corns), and *tunicata* (pod corns). The main variety consumed in the Union is the flat white dent corn, and the yellow dent is used for stock and fowl food. Percentage analyses of the most important varieties are as follows:—(*a*) *Zea mays indentata*, white dent, and (*b*) *Zea mays indurata*, yellow flint; moisture, (*a*) 10·93, (*b*) 10·46; oil, (*a*) 3·04, (*b*) 3·01; protein, (*a*) 10·93, (*b*) 10·28; fibre, (*a*) 2·13, (*b*) 2·06; ash, (*a*) 1·18, (*b*) 1·01; pentosans, (*a*) 4·57, (*b*) 4·49; starch, by diff., (*a*) 67·22, (*b*) 68·69; total phosphorus, (*a*) 0·36, (*b*) 0·32; organic phosphorus, (*a*) 0·31, (*b*) 0·28; inorganic phosphorus, (*a*) 0·05, (*b*) 0·04; ash from kernel, (*a*) 1·18, (*b*) 1·01; iron in

ash, (*a*) 3·88, (*b*) 3·38; iron in kernel, (*a*) 0·045, (*b*) 0·034; total protein, (*a*) 10·93, (*b*) 10·28; prolamin (alcohol-soluble), (*a*) 4·86, (*b*) 4·90; glutelin (alkali-soluble), (*a*) 3·10, (*b*) 3·10; globulin, (*a*) 0·38, (*b*) 0·10; methylpentosans, (*a*) 0·60, (*b*) 0·60; combined fatty acid in farinose, as percentage of dry starch, (*a*) 0·604, (*b*) 0·604. The analyses of maize oil, (*a*) freshly expressed, and (*b*) refined in the laboratory, deodorised, but not demargarinated, showed: Sp.gr. at 15·5/15·5° C., (*a*) 0·924, (*b*) 0·9225; n_D^{40}, (*a*) 1·4660, (*b*) 1·4658; saponification value, (*a*) 192·0, (*b*) 191·3; iodine value, Wijs, (*a*) 118·7; (*b*) 119·1; Reichert–Meissl value, (*a*) 4·20, (*b*) 0·20; Polenske value, (*a*) 1·20, (*b*) 0·37; acid value, as oleic per cent., (*a*) 3·12, (*b*) 0·05; ash, per cent., (*a*) 0·056, (*b*) 0·02; glycerol, per cent., (*b*) 10·34; unsaponifiable matter, per cent., (*a*) 1·85, (*b*) 1·45; mean mol. equiv. of fatty acids, (*b*) 279·5; titre of fatty acids, (*b*) 17·9° C.; iodine value of liquid fatty acids, (*b*) 143·0. The average percentage composition of Grade No. 4 (U.S. Official Grain Standards), the quality of maize most commonly used in the American industry, is: Moisture, 11·6; oil, 5·20; protein, 10·40; starch, 54·8; other carbohydrates, 14·33; fibre, 2·09, and ash, 1·52. The standard for this grade is: minimum weight per bushel, 49 lbs.; foreign matter and cracked corns, 5 per cent.; moisture, 19·5 per cent.; maximum limits of damaged kernels—heat damage, 0·5 per cent.; total, 8 per cent.

D. G. H.

Determination of the Extract in Wine. C. von der Heide and W. Zeisset. (*Z. Unters. Lebensm.*, 1935, **69**, 138–145.)—The direct determination of the extract of wine is subject to various errors, since, during the determination, acetic acid and its homologues are largely lost, part of the lactic acid is evaporated, malic acid is partly converted into malo-malic acid, the total acid-content diminishes considerably owing to ester-formation with the glycerol, and sugars are decomposed to some extent. When the residue obtained is dissolved in water to the original volume, the solution has a specific gravity markedly lower than that of the wine freed from alcohol. Indirect estimation of the extract from the specific gravity of the alcohol-free wine avoids these errors almost entirely. In different countries different tables are used for the relation between specific gravity and extract-content, but the values given by any one table are all comparable. With normal wines indirect determination gives higher (by 1·5 to 2 g. per litre) values than direct determination, but with wines adulterated with glycerol the reverse may hold. A series of measurements has been made on a 1931 Geisenheimer wine to determine the effects of various additions of glycerol and of lactic acid—the two commonest adulterants of wine—on the results of the determination of the extract. As the amount of glycerol added was increased, the difference between the direct and indirect extracts gradually diminished to zero and changed sign when 6 g. of glycerol per litre was introduced. Wines highly adulterated with glycerol yield residues which remain semi-liquid on the water-bath and in the drying-oven (at 100° C.), and solidify only on cooling.

The quantitative effects of glycerol and of lactic acid recorded by previous authors are confirmed. Addition of 1 g. of glycerol per litre of wine increases the extract, found indirectly, by about 0·6 g. per litre, and 1 g. of lactic acid per litre raises the extract by about 0·65 g. per litre. When both glycerol and relatively

large amounts of lactic acid are added, the difference between the direct and indirect extracts differs little from that found when the glycerol alone is added. In the discussion of the above results, the usefulness of extract determinations made in both ways in judging of the genuineness of a wine is emphasised.

T. H. P.

Composition of Commercial Palm Oils. IV. Progressive Hydrogenation as an Aid in the Study of Glyceride Structure. A. Banks, H. K. Dean and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1935, **54**, 77–82T.)—The glyceride structures of two palm oils—a native Cape Palmas and a Belgian Congo plantation oil—have been studied as representative of the extremes so far observed in fatty acid composition. The component acids of the two oils were respectively: myristic, 1·6, 1·3; palmitic, 32·3, 41·4; stearic, 5·5, 4·7; oleic, 52·4, 42·9; and linolic, 8·2 and 9·7 per cent. The oils were hydrogenated at 80° C. to varying extents, and the glyceride structures of the products were compared by calculation (except where linolic acid was still present) from the iodine value of the hydrogenated fat and the ester-fractionation analysis of the acids in the original oil. In several cases independent ester-fractionation analyses were carried out on the acids from the hydrogenated oils. Each of the partially hydrogenated fats and the original oils were also oxidised with potassium permanganate in acetone in quantities sufficient to yield the fully-saturated glycerides in amounts adequate for ester-fractionation analysis of their component acids. Where desirable, fractional crystallisation of the fully-saturated glycerides was carried out, to which process the fully-hydrogenated fats were also submitted.

The Cape Palmas oil (*a*) and the Belgian Congo oil (*b*) contained approximately (in percentages): tripalmitin (*a*) 2·0, (*b*) 5·5; dipalmitostearin (*a*) 1·5, (*b*) 1·0; dipalmito-"oleins" (*a*) 16·5, (*b*) 29·5; monopalmitodi-"oleins," including any palmitostearo-"olein," (*a*) 66·0, (*b*) 58·0; tri-C_{18}-glycerides (tri-"olein," or stearodi-"oleins") (*a*) 14·0, (*b*) 6·0. Palm-oil contains both α- and β-palmitodi-C_{18}-glycerides and both α- and β-mono-C_{18}-dipalmitins. The symmetrical forms (β-palmitodi-"olein" or β-"oleo"-dipalmitin) predominate, but there is evidence of increasing proportions of the unsymmetrical configurations (α-palmitodi-"olein" or α-"oleo"-dipalmitin), as the total amounts of palmitic and C_{18}-acids in the whole fat tend towards equality. The proportion of the unsymmetrical forms is thus definitely greater in the Belgian Congo oil than in the Cape Palmas oil. Any differentiation between linolic, oleic and stearic glycerides as such is not possible by the progressive hydrogenation method, but the proportions of stearic acid in the original fat in both oils are more consistent with the tri-C_{18}-glycerides being stearodi-"oleins" rather than tri-"oleins," and it is probable that tri-unsaturated glycerides are not present in any important amounts. The glyceride composition of the Belgian Congo palm oil (and consequently of other plantation oils, and also of native oils of Lagos, Bonny Old Calabar, Nigeria, Cameroons, etc.) would thus be roughly: fully saturated 7 (mainly tripalmitin with 1 to 2 per cent. of dipalmitostearin); "oleo"-dipalmitins, 29; "oleo"-stearopalmitins, 6; palmitodi-"oleins," 52; and stearodi-"oleins," 6 per cent.

D. G. H.

Ucuhuba Fat. A. Steger and J. van Loon. (*Rec. Trav. Chim. Pays-Bas*, 1935, **54**, 149–157.)—Two samples were examined: (1) A commercial product, supplied as a granular, yellow mass, not completely soluble in petroleum spirit and containing resin; (2) a sample extracted from the ground kernels of *Virola surinamensis* Warb., and separated into purified fat and resin. The kernel formed 86 per cent. of the whole nut and weighed, on the average, 1·43 g.; the total extract (oil + resin) amounted to 71·3, and the resin to 6·2 per cent. of the weight of the kernel. Sample (1) yielded 6·4 per cent. of resin on purification. The constants were as follows:

	Commercial sample			Extracted sample	
	Total	Purified	Resin	Fat	Resin
Sp.gr. at 78°/4° C.	0·9016	0·8855	—	0·8882	—
Iodine value (Wijs)	17	12·3	40	10·9	—
Thiocyanogen value	10·4	8·6	—	—	—
Saponification value	221	229	209	224	180
Acetyl value ..	234	—	244	—	—
Acid value ..	26·5	20·7	about 100	8·4	—
Reichert–Meissl value	1·5	1·5	—	1·6	—
Polenske value ..	3·9	4·6	—	4·0	—
n_D^{50}	1·4525	1·4502	1·5084	—	—
n_D^{70}	1·4445	1·4431	—	1·4446	—
M.p. °C.	47	47	—	51	—

The constants of the fatty acids (still containing some of the resin) of the crude commercial fat, the purified commercial fat, and the extracted fat were, in order: Iodine value (Wijs), 9·7, 10·6, 9·7; thiocyanogen value, —, 8·1, —; n_D^{70}, 1·4312, 1·4310, 1·4322; saponification value, 236, 236, 236; mean molecular weight, 238, 238, 238; m.pt., 47, 47, 48° C. The percentage composition of the fatty acids was: lauric, 12·6; myristic, 63·2; palmitic, 8·4; stearic, 1·5; 9:10-oleic, 6·3; linolic acid, 2·8; resinous matter, 5·2. The resin is composed of fatty acids (including hydroxy-acids) or their esters, unsaponifiable matter, and probably a little wax-like material. T. H. P.

Structure of the Cell-wall of Coffee. K. Täufel and H. Thaler. (*Z. Unters. Lebensm.*, 1935, **69**, 152–158.)—The cell-wall material of a Santos coffee containing 10·4 per cent. of moisture was obtained by extracting the coffee successively with ether and water, which removed respectively 16·1 and 31·3 per cent. of the original dry matter. The dry cell-wall material contained 0·43 per cent. of ash and formed 52·6 per cent. of the dry matter of the coffee, this being made up of: furfural, 1·6; loss on treatment with chlorine dioxide, 5·6; "glucose" constituent, 47·0 per cent. The "glucose" constituent contained: Mannan, 15·3; xylan, 1·8; and cellulose, 29·9. The matter lost on treatment with chlorine dioxide was not merely encrusting material, but comprised also protein and mineral matter. The figure given for cellulose represents actual cellulose and not "crude fibre." T. H. P.

Carbon Tetrachloride in Chloroform. E. Host Madsen. (*J. Pharm. Chim.*, 1935, **21**, 246–247.)—For the identification of carbon tetrachloride in chloroform the Danish Pharmacopoeia uses the following method:—From a

distilling-flask fitted with a fractionation column, 20 g. of the chloroform are distilled until about 1 ml. is left in the flask. One g. of this residue, when shaken with 150 g. of water, should dissolve completely. If 1 per cent. of carbon tetrachloride is present, a very slight opalescence is formed. With 2 per cent. the solution is definitely opalescent, and with 3 per cent. insoluble droplets can be seen. If the procedure is modified so that the residue is only 0·5 ml., and this is shaken with 150 g. of water, a definite opalescence is obtained in the presence of only 1 per cent. of carbon tetrachloride. S. G. S.

Biochemical

Biochemical Method for Determining Indigestible Residue in Faeces. R. D. Williams and W. H. Olmsted. (*J. Biol. Chem.*, 1935, **108**, 653–666.)—The non-digestible residue is defined as vegetable matter not attacked by digestive enzymes in the mammalian gut and consisting of lignin, cellulose and non-water-soluble hemicelluloses. For the determination of this, stools are collected and weighed. The wet weight is multiplied by 4, this amount of water is added, and the mixture is diluted to the nearest 25-ml. mark, transferred to a suitable ball-mill and ground for 20 minutes, or until the suspension will pass a 20-mesh sieve. Brisk rubbing may be necessary to sieve it. Into a 50-ml. glass-stoppered container are placed 25 ml. of the suspension, the stopper is inserted loosely, and the whole steam-sterilised at 15 lbs. per sq. in. for 30 minutes in order to kill the spores and to gelatinise the starch. After sterilisation, the material is cooled to below 50° C., and 20 ml. of bile-salt buffer solution, 5 ml. of pancreatin and sodium chloride solution and a few drops of toluene are added. The material is well mixed and incubated for 3 days at 45° C., with occasional shaking. The digest is filtered through a 125-mesh silk cloth, the digest being added slowly, with, at the same time, a stream of water from a wash-bottle. The residue is washed with 200 ml. of water, then with 50 ml. of hot ethyl alcohol, followed by 25 ml. of hot benzene and finally 25 ml. of ethyl ether. The residue is then transferred to a 50-ml. glass-stoppered container, which is placed in an oven at 70° C. for 2 hours, or until the residue is dry. To this prepared material 20 ml. of chilled 21·4 *N* sulphuric acid are added, and the whole is shaken briskly and put into an ice-box at 6°–10° C. The container is kept in the ice-box for 24 hours and shaken hourly (particularly during the first 5 hours). At the end of this time distilled water is added rapidly until the volume is 300 ml. (1·426 *N* acid). The mixture is heated and kept gently boiling under a reflux condenser for 3 hours. It is then cooled to room temperature, filtered through a loose layer of ignited asbestos in a Gooch crucible, and washed thoroughly with distilled water. The first 50 ml. of the washings are collected and added to the filtrate. The residue is further washed with 100 ml. of water, followed by adequate washings with alcohol, benzene and ether, then dried at 110° C., weighed, ignited, and re-weighed, and the loss of weight is calculated as lignin. The filtrate is neutralised with 50 per cent. sodium hydroxide solution to phenol-red and further diluted to 500 ml. The total reduction is determined by the Shaffer–Somogyi copper reagent (*J. Biol. Chem.*, 1933, **100**, 695). A portion (40 ml.) is fermented by the Somogyi washed-yeast procedure (*J. Biol. Chem.*, 1928, **78**, 117),

and the non-fermentable reduction is interpreted on the xylose-arabinose curve and multiplied by the factor 0·88 to convert pentose to pentosan. The fermentable reduction is interpreted on the glucose curve and multiplied by the factor 0·90 to convert glucose to cellulose. The pancreatin and sodium chloride solution is freshly prepared each day. To 100 ml. of 8·5 per cent. sodium chloride solution, 10 g. of pancreatin (U.S.P.) are added, and the solution is shaken for 30 minutes and filtered. The bile-salt buffer solution is prepared by mixing 20 ml. of 0·2 *M* potassium acid phosphate solution, 23·4 ml. of 0·4 *N* sodium hydroxide solution, 6·6 ml. of water and 2·0 g. of sodium taurocholate. The *p*H on final dilution should be 8·0 without the taurocholate. S. G. S.

Excretion of Copper in Urine and Faeces and its Relation to the Copper Content of the Diet. S. L. Tompsett. (*Biochem. J.*, 1934, **28**, 2088–2091.)—The use of amyl alcohol in the determination of copper by means of sodium diethyldithiocarbamate, as recommended by the author (*Biochem. J.*, 1934, **28**, 1544) has been extended to the determination of copper in urine, faeces and diets. For urine, 50–100 ml. are boiled almost to dryness with 5 ml. of concentrated nitric acid in a Kjeldahl flask. To the residue 2 ml. of strong sulphuric acid are added, and heating is continued to drive off the nitric acid. The remainder of the organic matter is destroyed by perchloric acid. The digest is made up to a known volume with water, and an amount containing about 0·01 mg. of copper is taken (about 50 ml. urine). To this 5 ml. of 20 per cent. sodium citrate solution are added, followed by 2 ml. of 4 per cent. sodium pyrophosphate solution. The mixture is made alkaline to litmus with ammonia solution, and 5 ml. of amyl alcohol and 0·5 ml. of 2 per cent. sodium diethyldithiocarbamate solution are added. The whole is well shaken, and the amyl alcohol layer is removed, filtered and compared in a colorimeter with a standard containing 0·01 mg. of copper. For the faeces, 1 g. of dried material is heated with 5 ml. of concentrated sulphuric acid and 15 to 25 ml. of perchloric acid until all the organic matter is destroyed. The excess of perchloric acid is then removed, and the mixture is cooled and diluted to 100 ml. If any white insoluble matter is present, the digest is diluted to 20 ml. with water, 1 ml. of concentrated hydrochloric acid is added, and the whole is heated until solution is complete, after which it is diluted to 100 ml. A volume containing 0·01 mg. of copper (about 10 ml.) is treated as for urine, except that 5 ml. of the sodium pyrophosphate solution are used. In the case of the diets 10 g. of the dried material and 5 g. of copper-free sodium phosphate are ignited together in a silica basin at as low a temperature as possible. Final traces of carbon are removed by treatment with concentrated nitric acid and heating. The ash is dissolved in distilled water containing 5 ml. of concentrated hydrochloric acid, and the solution is diluted to 50 ml. The analysis is carried out in the same manner as for the faeces. It is found that an average daily diet for humans contains 2 to 2·5 mg. of copper, and that the urine contains 0·08 to 0·48 mg. per litre.
S. G. S.

Chemical Method for Estimating Epinephrine (Adrenaline) in Blood. J. C. Whitehorn. (*J. Biol. Chem.*, 1935, **108**, 633–643.)—The method depends on the use of silicic acid for the separation of epinephrine from other reducing

substances, and also on a sensitive arsenomolybdic acid reagent for colorimetric assay. The reagent is not specific for epinephrine, which must therefore be purified by the silicic acid treatment. The arsenomolybdic reagent is prepared by dissolving 60 g. of crystalline sodium molybdate and 10 g. of crystalline sodium arsenate in 250 ml. of water. The solution is filtered, to the filtrate and washings 5 ml. of bromine water are added, and the liquid is diluted to 500 ml. For use, 100 ml. of this solution are mixed with 8 ml. of concentrated sulphuric acid. The silicic acid is prepared by mixing 20 g. of finely granular precipitated silica with 60 ml. of dilute (1:1) sulphuric acid in a 500-ml. flask. The mixture is boiled for 10 to 15 minutes, with constant whirling. When cool, the supernatant liquid is decanted, and the silicic acid is washed by decantation ten or twelve times with 100-ml. portions of water. The residue is finally filtered and dried on a Buchner filter. A solution of 5 g. of anhydrous sodium sulphite in 50 ml. of water is also prepared and centrifuged. Just before use 5 ml. of this solution are mixed with 35 ml. of dilute (1 : 1) sulphuric acid. In addition, a phosphate buffer solution is required, and this is prepared by dissolving 17·4 g. of dipotassium phosphate and 6·8 g. of monopotassium phosphate in 100 ml. of water and filtering the solution. The ultimate standard is epinephrine; but, as weak solutions of this are unstable, it is convenient to use catechol instead, $10m\mu$ of catechol giving a colour equal to that of $5m\mu$ of epinephrine. The stock solution is made by dissolving 1 g. of crystalline catechol in water, adding 20 ml. of a 10 per cent. solution of anhydrous sodium sulphite and 100 ml. of *N* hydrochloric acid solution, and diluting to 1 l. Just before use some of the stock solution is diluted (1 to 500) with 0·4 *N* sulphuric acid solution. Five ml. of this weak solution will then contain $10m\mu$ of catechol. For the determination 7 to 10 ml. of blood are taken from the animal and transferred *at once* to a flask containing 50 ml. of 3 per cent. trichloroacetic acid solution. More of the acid solution is added gradually until the blood is diluted 10 times, when the mixture is shaken vigorously, allowed to stand for a period of from 15 minutes to several hours and filtered. While the blood solution is standing, a calcium chloride tube (approximately 20 mm. × 200 mm.) is prepared by making three small indentations about 7 mm. below the bulb. Into the space between the bulb and the indentations a small plug of cotton or glass wool is fitted. The tube is then attached to a suction-flask, and 5 ml. of silicic acid are added. The flask is attached to a filter-pump, and an arrangement such as a Hoffman clamp is also used, so that the fluid can be drawn through the tube at the rate of 3 drops per second. The silicic acid is washed with water and small portions (1 to 3 ml.) of sodium sulphite solution until the rinsings are neutral to bromthymol blue. Fifty ml. of the trichloroacetic acid filtrate (5 ml. of blood) and 3 drops of bromthymol blue solution are placed in a small flask and neutralised with approximately *N* sodium hydroxide solution. As soon as the *p*H reaches 7 or more, 1 ml. of the phosphate buffer solution is added immediately. This solution is then poured into the adsorption tube and sucked through the silicic acid at the rate of 3 drops per second. The tube and the silicic acid are rinsed with three successive portions of 8 ml. of recently boiled and cooled distilled water. Air must not be sucked through the tube. The adsorption tube is then removed, and a clean, dry, 15-ml. centrifuge tube is placed in the

filter-flask. The centrifuge tube is fitted with rubber tubing at the bottom, so that it comes well up into the neck of the flask. The adsorption tube is now replaced, and 5 ml. of 0·67 *N* sulphuric acid solution are added. The tube is twirled to suspend the silicic acid, and the suspension is sucked into the centrifuge tube. Into a test tube (A) 5 ml. of the solution from the centrifuge tube are placed. Into a second tube (B) 5 ml. of the 1:500,000 catechol solution, and into a third tube (C) 5 ml. of a solution containing no epinephrine, but of acidity 0·4 *N*, are also placed. Into each of three tall test-tubes (1, 2 and 3) marked at 25 ml., are pipetted 2 ml. of the arseno-molybdic acid reagent, and the tubes are placed in a boiling water-bath for 5 to 10 minutes. Five ml. of the sulphite and sulphuric acid mixture are added rapidly to tube A, and the solution is mixed quickly and poured into tube (1). Tube A is rinsed once with the resulting mixture, which is poured back into tube (1), and placed in the boiling water-bath for exactly 3 minutes. Tubes B and C are treated in the same way. At the end of 3 minutes the tubes are transferred to a beaker of cold water and allowed to stand for 15 minutes or longer. The standard solution is diluted to 25 ml. and compared with the undiluted unknown and blank in a colorimeter. If the material to be tested differs from the blank by less than 0·02 mg. per litre, it should be counted negative, for a difference of this amount can be attributed to variability in the blank when the same reagents are used. S. G. S.

Relative Biological Efficiencies of the Vitamin *A* and Carotene of Butter. R. G. Booth, S. K. Kon and A. E. Gillam. (*Biochem. J.*, 1934, **28**, 2169–2173.)—No difference has been found in the vitamin *A* activities of butter from Shorthorn and Guernsey cattle during summer, autumn and winter feeding. The vitamin *A* and carotene contents of the butter were determined spectrophotometrically, and it was found that these varied considerably in the two breeds, although the total biological activity was the same. From these results it has been possible to calculate that the vitamin *A* activity of butter is about six times that of the carotene when measured by its growth-promoting action. S. G. S.

Agricultural

Effect on Fruit of Fumigation with Hydrocyanic Acid. F. Beran. (*Z. Unters. Lebensm.*, 1935, **69**, 170–174.)—Zyklon-B, a commercial product largely used for the fumigation of fruit (*cf.* ANALYST, 1933, **58**, 775), consists essentially of hydrocyanic acid absorbed in a carrier (kieselguhr, etc.), but contains also an irritant which affects the mucous membrane, and thus gives warning of its presence. Irritants of lower and higher vapour pressures than hydrocyanic acid are used, the latter indicating the presence of the hydrocyanic acid at the beginning of the fumigation, and the former becoming perceptible only after its completion. Zyklon-B contains a little ethyl or methyl chlorocarbonate, but its main irritant is methyl bromoacetate. Experiments with apples show that fumigation for periods up to 2 hours with either hydrocyanic acid (12 g. per cu. metre) or methyl bromoacetate (0·2 g. per cu. metre) does not injure the fruit. When, however, the two compounds are used together, 40 per cent. of the fruit show damage after

1 hour (at 18° C.), 60 per cent. after 2 hours, and 80 per cent. after 3 hours. This result is found to be due to the fact that the methyl bromoacetate intensifies the respiration of the fruit, so that increased quantities of hydrocyanic acid are absorbed. The use of calcium cyanide preparations, which yield hydrocyanic acid under the influence of atmospheric moisture, is, therefore, to be preferred to that of products of the Zyklon-B type. T. H. P.

Determination of Mono-calcium Phosphate by means of Urea. C. W. Whittaker, F. O. Lundstrom and W. L. Hill. (*J. Assoc. Off. Agric. Chem.*, 1935, **18**, 122–127.)—The method is based on the reaction of urea with mono-calcium phosphate according to the equation

$$Ca(H_2PO_4)_2.H_2O + CO(NH_2)_2 = H_3PO_4.CO(NH_2)_2 + CaHPO_4 + H_2O,$$

and depends on the fact that urea phosphate is soluble in alcohol, whilst calcium hydrogen phosphate is not. There are three main operations: (*a*) the treatment of the sample with a large excess of urea to ensure that the reaction goes to completion, (*b*) the precipitation of the calcium hydrogen phosphate from the mixture by the addition of alcohol, (*c*) the determination of phosphoric acid in the solution of urea and urea phosphate. Details of the method are as follows: To the sample (2 g. for mono-calcium phosphate, or 4 g. for ordinary or double superphosphate), ground to about 100-mesh fineness, and contained in a 100-ml. volumetric flask, are added 50 ml. of urea solution (90 g. of urea in 100 ml. of water), and the liquid is shaken mechanically or intermittently by hand for 4 hours, after which it is diluted to 100 ml. and filtered immediately. To a 25-ml. portion of the filtrate are added 75 to 100 ml. of 95 per cent. alcohol, the mixture is well shaken and filtered, and the precipitate is washed with 300 to 350 ml. of alcohol. The filtrate is diluted to 500 ml. with water, a 25-ml. portion of this filtrate is evaporated to dryness, and the organic matter is destroyed by adding 5 ml. of hydrochloric acid and 25 ml. of nitric acid, and again evaporating to dryness, this process being repeated if necessary. The residue is dissolved in 10 ml. of nitric acid and a little water, and the solution is neutralised with ammonia and rendered slightly acid with nitric acid. After dilution of the solution to 75 ml. the phosphoric acid is determined according to *Methods of Analysis, A.O.A.C.*, 1930, **16**, 10(*a*). The P_2O_5 found, multiplied by 2, gives the P_2O_5 present as mono-calcium phosphate. With samples containing free phosphoric acid, this free acid must be determined separately by a suitable method (*J.A.O.A.C.*, 1934, **17**, 487) and subtracted from the P_2O_5 found. S. G. C.

Organic

Iodine Values of Linolenic, Linolic and Stearolic Acids by the Wijs and Rosenmund-Kuhnhenn Methods. Y. Toyama and T. Tutiya. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 32–35B.)—The Wijs and Rosenmund-Kuhnhenn methods for determining iodine values were applied to linolenic and linolic acids, as the commonest polyethylenic acids in vegetable oils, and to stearolic acid, which has a triple linkage. With the first two acids, excess of reagent in the Wijs method has little effect on the value, particularly with linolic acid (unlike the values

obtained for the highly unsaturated sardine-oil acids), and in the Rosenmund–Kuhnhenn method the influence of excess of reagent is still less noticeable, although the iodine values are lower by this method [272 (Wijs), 264·6 (Rosenmund–Kuhnhenn) for linolenic, and 181 and 176·7, respectively, for linolic acid]. Taking into account values previously obtained with highly unsaturated acids, it is concluded that the Wijs method gives higher iodine values than the Rosenmund–Kuhnhenn method for the polyethylenic acids, and that the discrepancy between the methods increases with increase in the degree of the unsaturation, being largest in the case of the unsaturated acids of sardine oil and very small for linolic acid. With stearolic acid the Wijs method gives an iodine value corresponding to the absorption of 1 ml. of halogen, whilst results with the Rosenmund–Kuhnhenn method are influenced by the amount of excess of the reagent and are always higher than the value calculated for addition of 1 ml. of halogen. D. G. H.

China Jute Seed and Oil. T. Inaba and K. Kitagawa. (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 77B.)—The China jute plant (*Abutilon avicenne* Garten; *Sida tiliafolia* Fisch. N.O. *Malvaceae*) is cultivated in Manchuria for the fibre. The weight of 100 seeds was 1·568 g., and their percentage composition was as follows:—Oil, 18·30; moisture, 10·29; nitrogen, 2·96; fibre, 14·03; ash, 5·55; P_2O_5, 2·56. The constants for the oil were: Sp.gr. at 15/15° C., 0·9281; n_D^{20}, 1·4769; saponification value, 190·3; iodine value, 139·0; acid value, 0·84; acetyl value, 16·3; Hehner value, 95·72; insoluble bromide, trace; unsaponifiable matter, 0·62 per cent. D. G. H.

Determination of Sulphuric Acid in Wool. J. Barritt. (*J. Text. Inst.*, 1935, **26**, 87–92T.)—A sample of carded, carbonised wool, weighing 2 g., is steeped in 100 ml. of distilled water in a tared flask, 10 ml. of 10 per cent. pyridine solution being then added and the contents of the flask made up to a suitable weight (*e.g.* corresponding with 150 to 250 ml.). The mixture is shaken well and allowed to stand for 1 hour, and suitable aliquot portions (*e.g.* 50 ml.) are removed and titrated with 0·1 *N* sodium hydroxide solution, with phenolphthalein as indicator. Details are given of the method of preparation of acid-free wool to which various known quantities of sulphuric acid were added in order to test the method, and it is shown that recovery is almost theoretical. Comparisons were also made with the terephthalic acid and triethanolamine methods (Trotman and Gee, *J. Soc. Dyers and Col.*, 1932, **48**, 321), but the results indicated that the acid was not distributed evenly throughout the wool. The pyridine method is preferred because, unlike the triethanolamine method, it is not empirical and does not give higher results with an increase of the excess of reagent, while the terephthalic acid method requires correction by a blank determination, and even then gives slightly low results. J. G.

Stains to Distinguish Fibroin and Silk Gum. W. S. Denham and E. Dickinson. (*J. Soc. Dyers and Col.*, 1935, **51**, 93–97.)—Sections are prepared (*cf.* Kultschicky, *Z. für wiss. Mik.*, 1887, **4**, 48) by winding 6 turns of raw silk on a wire frame and immersing them in a thick solution of "celloidin" in a mixture of

ether and alcohol for 24 to 48 hours, followed by immersion for a few minutes in chloroform. When the solvent has volatilised the frame is embedded in paraffin wax (m.p. 130° C.), and sections 0·006 mm. thick are cut and, with the aid of warm water, are flattened on a slide smeared with glycerin-albumin. The slide is dried and washed in succession with xylene and a mixture of ether and alcohol to remove the paraffin and celloidin, complete removal being essential. Some of the silks were first degummed, and in this case a hank weighing 0·5 g. was treated in succession with 1 and 0·5 per cent. solutions of soap for 1 hour at 95° to 98° C., with an intermediate wash in warm water and a final wash in cold water. Poor results were obtained with 1 per cent. solutions of ruthenium red, although, after 5 to 20 hours, the gum had a deeper crimson shade than the fibroin. Picrocarmine (0·1 per cent. solution, 1 to 48 hours) gave a red to brown colour with gum silk, and yellow with degummed silk (*cf.* Wagner, *Melliand Textilber.*, 1925, **6**, 43, 118). Cyanine (quinoline blue) solution, prepared according to Herzog (*id.*, 1932, **13**, 121, 181) by dilution of a saturated solution to twice its volume with water, and then with one-third of the total volume of glycerin, gave deep blue and pale blue with gum and fibroin, respectively, after 2 hours. Azolitmin (0·1 per cent. of dye with 0·1 per cent. of sodium hydroxide for 24 hours) gave a blue stain with gum silk, but no stain with degummed silk (*cf.* Wagner, *loc. cit.*). Colours produced with 0·1 per cent. solutions of new stains are for gum and fibroin, respectively:— Benzopurpurine-4BS for 30 minutes, red to pink, pale pink to yellow; chlorazol purpurine-10BS for 30 minutes, orange-red to brown, pink; anthracene acid brown-G with 0·1 per cent. sulphuric acid for 30 minutes, golden brown, paler brown; diamine brown-B with acid for 30 minutes, chocolate brown, fawn; diamine green-G, with 0·1 per cent. sodium hydroxide solution for 45 minutes, dark green, pale green; acid magenta-N for 30 minutes, red-brown, blue-red; methylene blue-R (conc.) with alkali for 1 minute, blue-black, royal blue; alizarin delphinol-SEN for 30 minutes, dark green and light blue with hanks, and after 24 hours, blue-black and pale blue with sections. The results were similar for white or yellow hanks. Residual gum in degummed silk can be detected by means of azolitmin (which is slow in action), cyanine (which stains calcium soap and gum the same colour), benzopurpurine-4BS, picrocarmine, chlorazol purpurine-10BS and acid magenta-N. Beads produced by gassing are stained in the same way as sericin, but are easily recognisable by their shape. The results apply equally to white or yellow silks, but slight differences in shade are obtained according as hanks or sections are used. Addition of acid or alkali to the stain had either no effect or gave improved results (as indicated), but it should be avoided if possible with sections, as it renders manipulation more difficult. J. G.

Determination of Lignin. I. Errors introduced by the Presence of certain Carbohydrates. II. Errors introduced by the Presence of Proteins. A. G. Norman and S. H. Jenkins. (*Biochem. J.*, 1934, **28**, 2147–2159, 2160–2168.) —I. In the determination of lignin by the method involving the use of 72 per cent. sulphuric acid, several disturbing factors are present. The apparent lignin figure is increased by certain sugars, such as xylose and fructose, which give an insoluble residue when treated with 72 per cent. sulphuric acid. Polysaccharides containing

pentoses and sucrose (presumably owing to its fructose unit) give similar residues. This disturbance has a time-factor, and at 2 hours the effect is small. Because of the presence of xylose, the figures usually quoted for lignin are too high, but this can be corrected, either by reducing the contact-time to 2 hours, or by pre-treatment with dilute mineral acids, although the latter method is of doubtful value, since the action of dilute acids on lignin is unknown. With pentoses the disturbance is probably due to the slow formation of furfuraldehyde and its condensation with lignin to form an insoluble phenol-furfuran resin.

II. Although proteins by themselves do not give a precipitate on standing with 72 per cent. sulphuric acid, yet, when they are added to vegetable matter, the lignin-content is apparently increased, and the residue contains nitrogen. This increase is probably due to the union of protein fission-products with lignin. If the nitrogen in the lignin is determined, calculated as protein, and a correction employed, an even greater error is often introduced. The reduction of the time of contact with acid from 16 hours to 2 hours, or the use of the Ritter–Seborg–Mitchell procedure (*Ind. Eng. Chem., Anal. Edit.*, 1932, **4**, 202), does not reduce the error, but acid pre-treatment causes a reduction in most cases. When xylose and proteins are present together, treatment with 72 per cent. acid causes an insoluble precipitate to form if the amount of protein is small. As the amount of protein increases, the amount of the precipitate decreases, until, eventually, none is formed. The pre-treatment by acid hydrolysis is provisionally adopted. S. G. S.

Volumetric Method for the Determination of Free Sulphur in Rubber. A. F. Hardman and H. E. Barbehenn. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 103, 104.)—The method depends on the reaction of metallic copper with the sulphur in a medium of acetone, the copper sulphide produced being subsequently decomposed with hydrochloric acid, yielding hydrogen sulphide, which can be absorbed and determined volumetrically. The rubber sample (1 to 2 g.) is extracted with 50 ml. of acetone by boiling under reflux for about 6 hours, a spiral of copper gauze (obtained by coiling up a 18 × 0·25-inch strip of 40-mesh gauze), previously cleaned in boiling concentrated hydrochloric acid and dried, being present in the acetone during the extraction process. After removal of the acetone, the flask containing the sulphurised spiral, together with any copper sulphide which may have scaled off, is closed with a stopper carrying a thistle-funnel, a closed leading tube, and an exit-tube connected with an absorbing vessel containing 10 ml. of ammoniacal cadmium chloride solution (10 g. of cadmium chloride, 200 ml. of water, 300 ml. of concentrated ammonia); 20 ml. of concentrated hydrochloric acid are poured into the evolution flask, which is heated on a steam-bath for about 5 minutes until the copper sulphide is dissolved. The hydrogen sulphide is then swept through the apparatus by admitting a stream of air for 1 minute. The absorbing solution should remain ammoniacal. A sufficient quantity of 0·04 *N* potassium iodate-iodide solution, followed by 10 ml. of concentrated hydrochloric acid, is added to the absorbing solution, when the cadmium sulphide dissolves; the quantity of standard potassium iodate-iodide solution added must have been sufficient to insure that a permanent yellow colour, due to free iodine, remains at this stage. After 1 minute, the free iodine is back-titrated

with 0·04 *N* thiosulphate solution, starch being used as indicator. In six test-experiments with 0·01 g. of elemental sulphur in the absence of rubber, results varying from 0·00990 to 0·01007 g., with an average of 0·01001 g., were obtained.

S. G. C.

Sulphate "Pictures" as a Means of Identifying Inks and Estimating the Relative Ages of Writing. W. Heess. (*Archiv. für Kriminologie*, 1935, **96**, 13–17.)—The method is an improvement on that suggested by Heess, Mezger and Rall (*id.*, **92**, 107), and depends on the fact that the combined sulphuric acid contained in most inks gradually diffuses away from the ink-stroke into the surrounding paper over a long period of time. This penetration is rendered visible as follows:—The paper is bathed in a solution containing 5 per cent. each of lead perchlorate and perchloric acid, which produces lead sulphate from the sulphuric acid present in the paper, and, since this compound is insoluble in perchloric acid, fixes it in the fibres. The iron salts in the ink also dissolve, at a rate which depends on the age of the writing, in 5 to 30 minutes. Any aniline dyes present in the ink must then be decolorised by addition to the mixture of 1 drop of a 1 per cent. solution of potassium permanganate, excess of which is at once removed by the action of water saturated with lead sulphate and containing a few drops of a 10 per cent. solution of hydrazine hydrochloride. The liquid is then poured off, and the paper is immersed in lead sulphate water for 10 minutes, and then washed with distilled water. The specimen is finally immersed in a solution containing 0·5 per cent. each of sodium sulphide and potassium hydroxide, which converts the lead on the fibres into lead sulphide. The paper is then again washed in distilled water, and finally in conductivity water for 15 minutes. An application to a case of suspected false entry in a health-insurance register is described, and photographs illustrate the writing (1) after 9 months, showing a faint stroke of normal width with sharp contours; (2) after 21 months, showing a rather wider and more intense line with more diffuse contours; (3) after 23 months, showing a further stage in diffusion of the acid; and (4) after 45 months, showing a blurred line twice its original width. It is possible to distinguish (1) from (2), (3) and (4), and also (2) from (4), but not (3) from (4). It is desirable that the specimens compared should be written on the same paper, as this influences the degree of spreading. In the case of wood paper, which contains variable quantities of sulphate, this is particularly important. It is also essential that all the specimens should have been stored under the same conditions of temperature and humidity; an illustration shows writing on paper which is believed to have been stored in an unheated room and which appears less blurred than (4), although it is 42 months old. Examination of the specimens is facilitated by ensuring that the treated and untreated specimens are adjacent parts of a common line, and by the use of a lens. Photographs (magnification 10 to 15) are conveniently taken with the aid of the Leitz Macro Ring Illuminator with a Summar 24 or 35 lens, and the use of panchromatic plates is advisable if the blank portions of the paper itself have become at all brown as a result of treatment.

J. G.

Benzoyl Auramine G. A New Indicator for Kjeldahl Determinations. J. T. Scanlan and J. D. Reid. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 125–126.)—Benzoyl Auramine G is said to be a somewhat more satisfactory indicator than methyl red or cochineal for Kjeldahl titrations. Good results were obtained with 0·15 ml. of a 0·25 per cent. solution in methyl alcohol added to 100 to 300 ml. of solution. The colour-change from violet to pale yellow is sharp, owing to the narrow *p*H range (5 to 5·6) of the indicator. When observed in daylight, an intermediate grey colour occurs between the violet and the yellow, indicating a *p*H value of 5·4; by tungsten lighting, the grey is not observed, but the main colour-change shows as clearly as in daylight. A disadvantage of the indicator is that it hydrolyses slowly, so that it should not be added to the solution until it is ready for the titration, which should be completed without delay. The new indicator can be prepared by benzoylating the free base of Auramine G (British Colour Index, No. 655); details of preparation are given in the original paper.

S. G. C.

Inorganic

Reactions of Mercuric Iodide. E. Montignie. (*Bull. Soc. Chim.*, 1935, **2**, 373–375.)—Mercuric iodide is converted into mercurous iodide when (1) heated with neutral sodium sulphite solution, (2) treated with stannous chloride, or (3) boiled with sodium formate solution. Mercury is precipitated if the iodide is treated with (1) hydroxylamine hydrochloride in presence of potassium hydroxide, (2) sodium hypophosphite in presence of hydrochloric acid, or (3) phenylhydrazine and zinc in presence of potassium hydroxide. Either mercurous iodide or mercury is obtained by the action of sugars on the iodide in presence of potassium hydroxide. When heated with dextrose, laevulose, arabinose or xylose (sometimes in the cold), the iodide yields mercury, whereas treatment with sucrose, mannitol or inositol gives a brown mixture of mercurous and mercuric iodides.

Silver nitrate readily decomposes mercuric iodide, yielding silver iodide and mercuric nitrate. Similar double decomposition occurs when the iodide is heated with solutions of alkali or alkaline-earth chlorides, or of the hydrochloride of aniline, pyridine, α-naphthylamine, benzidine or *o*-phenylenediamine. The only heavy metal chlorides reacting with mercuric iodide are stannous chloride (see above), and ferric chloride which, when heated, gives mercuric chloride, ferrous iodide and iodine. Cold sodium thiosulphate solution, either acid or alkaline, dissolves mercuric iodide with formation of the complex $I.Hg.S_2O_3Na$; when the solution is heated, the reaction $Na_2S_2O_3 + HgI_2 + H_2O \rightarrow HgS + HI + NaI + NaHSO_4$ proceeds rapidly in acid, and less readily in alkaline, solution. Potassium selenite or selenate does not react with mercuric iodide in an alkaline medium, but potassium tellurate is converted into the pale yellow basic mercuric tellurate, $HgTeO_4,2HgO$. Saturation of an alkaline solution of diethylmalonylurea (veronal) with mercuric iodide, followed by concentration on a water-bath, yields a white, crystalline compound, $C_{16}H_{22}O_6N_4Hg$. A similar reaction takes place with ethylphenylmalonylurea (gardenal), the compound $C_{24}H_{22}O_6N_4Hg$ being formed.

T. H. P.

Volumetric Determination of Iodine in Mercury Compounds. D. Köszegi and N. Tomori. (*Z. anal. Chem.*, **1935**, **100**, 257–259.)—The iodomercurate complex is decomposed by the following procedure:—The solution (about 25 ml.) is boiled for 1 to 2 minutes with 10 ml. of 2 *N* potassium hydroxide solution and 3 ml. of 40 per cent. formaldehyde. The precipitate of metallic mercury is filtered off, and the filtrate is neutralised to phenolphthalein with 0·1 *N* nitric acid and titrated with silver nitrate solution. W. R. S.

Determination of Molybdenum in Steel and its Separation from Tungsten. W. Werz. (*Z. anal. Chem.*, **1935**, **100**, 241–257.)—A critical study has been made of the determination of molybdenum in steel, and of the interference of tungsten. As regards the precipitation of molybdenum sulphide, the author confirms the fact that pressure precipitation with hydrogen sulphide is not necessary. The essential factor for complete precipitation is a very rapid current of the gas; this will quantitatively precipitate the metal, even from solutions containing phosphoric acid. Copper is the only other member of the hydrogen-sulphide group found in alloy steels; for its separation from molybdenum, the mixed sulphides are boiled for a few minutes with 20 ml. of 10 per cent. caustic soda. The filtrate from the copper sulphide is boiled with 5 ml. of ammonium sulphide solution, and the molybdenum sulphide is precipitated by excess of dilute sulphuric acid, collected, and ignited to trioxide.

Separation from tungsten.—With alloy steels containing tungsten and molybdenum, the precipitated tungstic acid always contains molybdenum, whether nitric acid or chlorate has been used as oxidiser. Molybdenum cannot be quantitatively separated as sulphide in phosphoric acid solution from substantial amounts of tungsten such as occur in high-speed steels: the precipitate always contains more or less tungsten, while the filtrate is never quite free from molybdenum. When tungsten and molybdenum are separated from iron, etc., by addition of the solution of the steel to a strong solution of sodium hydroxide (a single treatment at boiling heat ensures quantitative separation from iron), and the acidified solution is treated with tartaric acid and hydrogen sulphide, the precipitated molybdenum sulphide is not free from tungsten. Correct results, however, are obtained by addition of the tartaric acid to the strongly alkaline solution (which should remain alkaline; an acid solution treated with tartaric acid must next be treated with excess of alkali). It must be assumed that a stable tartaro-tungstic complex forms in the alkaline medium. The solution is now acidified with sulphuric acid and treated at 80° C. with a rapid stream of hydrogen sulphide. By the use of this procedure it is possible to determine molybdenum in alloy steels without eliminating the iron. The drillings (1 or 2 g.) are dissolved in 20 ml. of strong hydrochloric acid and 30 of water, the solution is oxidised with 15 or 30 ml. of 5 per cent. potassium chlorate solution, chlorine is boiled off, and 30 or 60 ml. of 30 per cent. tartaric acid solution are added, followed by excess of hot 20 per cent. caustic soda. An excess of sulphuric acid is then added, the deep brown colour changing to green, the solution is filtered and diluted to 300 ml., and the molybdenum is precipitated at 80° C. by a brisk stream of hydrogen sulphide. The quantity of molybdenum in the assay should not exceed 0·03 g.,

otherwise its precipitation as sulphide is liable to be incomplete. For tungsten-free steels the procedure is as follows:—One g. of drillings is dissolved in water (20 ml.), strong sulphuric (10 ml.), phosphoric (5 ml.), and 1:1 nitric (10 ml.) acids; the solution is evaporated until white fumes appear, cooled, diluted to 200 ml., and filtered. The filtrate is treated with a rapid stream of hydrogen sulphide for 15 minutes, and filtered after 20 minutes' standing, and the precipitate is washed with hydrogen sulphide water acidified with sulphuric acid, and ignited to trioxide. Copper, if present, must be removed as described above. W. R. S.

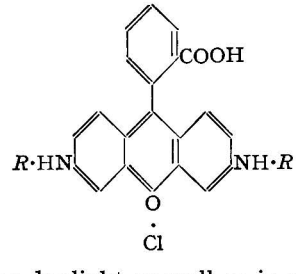
Calcium Hypochlorite as a Volumetric Oxidising Agent. Determination of Ammonia. I. M. Kolthoff and V. A. Stenger. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 79–81.)—The calcium hypochlorite supplied by an American manufacturer yields solutions which are sufficiently stable for use as a volumetric oxidising agent; when kept in blackened bottles, 0·1 *N* and 0·01 *N* solutions suffered only a slight loss in strength in several months. An advantage of hypochlorite is that it may frequently be used for titration in slightly alkaline solution, thus eliminating interference by chromate, bromate, etc. The solution may be standardised (*a*) indirectly, by adding potassium iodide to it, acidifying, and titrating the liberated iodine with standard thiosulphate solution, (*b*) by using it to titrate 25 ml. of standard sodium arsenite solution to which has been added 10 ml. of a solution containing 10 per cent. of potassium bromide and 5 per cent. of sodium bicarbonate, 0·05 ml. of a 0·2 per cent. aqueous solution of Bordeaux dye being added as indicator near the expected end-point; the colour change is from pink to a faint yellowish-green. *Determination of ammonia.*—To 25 ml. of the neutralised ammonia solution are added 10 ml. of a solution containing 10 per cent. of potassium bromide and 5 per cent. of sodium bicarbonate, together with a slight excess of standard hypochlorite solution. After about 5 minutes, the liquid is decolorised by the addition of standard sodium arsenite solution, and then titrated with the standard hypochlorite solution, Bordeaux red being used as indicator. From 0·5 to 20 mg. of ammonia may thus be determined, 0·1 *N* hypochlorite solution being used for the larger quantities, and 0·01 *N* for the smaller amounts. In test experiments, results within 3 per cent. of the theoretical were obtained, and, when disodium hydrogen phosphate was substituted for the sodium bicarbonate as a buffer, the method was found satisfactory in the presence of about 30 mg. of copper chloride, ferric chloride and potassium bromate, and of 10 mg. of potassium dichromate. S. G. C.

Rapid Test for Chlorate. H. R. Offord. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 93–95.)—A test-paper method has been devised for testing for chlorate in a few drops of solution. *Test-paper.*—No. 1 Whatman paper is soaked in 3 *N* ammonium thiocyanate solution and dried in a current of warm air at a temperature not exceeding 70° C. The dry paper may be kept without deterioration for several months if protected from light and dust. *Method.*—A drop of the solution to be tested is added to the paper, which has been dried before use at 60° C. for 10 minutes. The paper is supported on glass and placed in a drying oven at 95 to 105° C. for 5 to 30 minutes, the time required being the longer with small

amounts of chlorate. A yellow colour is produced when chlorate is present. The use of duplicate test-papers is advised. The smallest detectable concentration of chlorate (either the sodium, potassium or calcium salt) was found to be 0·01 mg. per ml. The colour produced varies from a pale lemon-yellow (0·01 to 1·0 mg. per ml.), through a lemon-chrome (1 to 10 mg. per ml.), to orange or cadmium-yellow (over 10 mg. per ml.). The yellow colour is chiefly due to canarine ($C_8H_8N_8OS_7$) and pseudothiocyanic acid ($C_3HN_3S_3$). Chlorate in concentration of 0·1 mg. per ml. can be detected when present in 0·1 *N* solutions of sulphuric, nitric, acetic and oxalic acids, or sodium hydroxide, and also in acid or alkaline solutions containing 100 mg. per ml. of sodium chloride. Cyanide, thiosulphate and sulphite tend to interfere when present in quantity greater than the chlorate. The presence of any appreciable quantity of iron masks the test, and halogens, bromate, iodate, hypohalites, persulphate, peroxide (but not perborate) and cupric salts yield colours similar to that given by chlorate. *Application to plant extracts.*—Among tests carried out, it was found that chlorate in concentration of 0·05 mg. per ml. added to *Nitella* expressed sap was readily detected, the pale yellow colour of the sap itself not interfering. Positive results for chlorate were obtained in unfiltered or unclarified cold-water extracts of 1-g. samples of roots, stem, leaves and petioles of *R. petiolare*, when the plants had previously been soaked in dilute sodium chlorate solution, extracts of the untreated plants giving no interfering colour. S. G. C.

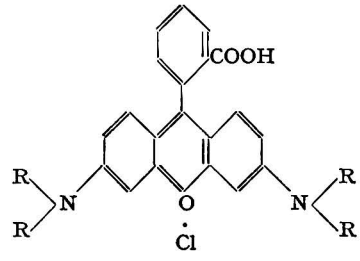
Microchemical

Spot Tests for Organic Compounds. VI. F. Feigl, V. Anger and R. Zappert. (*Mikrochem.*, 1934–35, **16**, 67–79.)—TEST FOR ALIPHATIC AND AROMATIC AMINES WITH FLUORESCIN CHLORIDE.—Many compounds containing the NH_2–, NH–, or NCH_3– group, when fused with fluorescin chloride and anhydrous zinc chloride, give dyestuffs of the rhodamine group. The nature of the dye varies with the different types of amines, and the reaction has been adopted as a test for their differentiation:—(i) *Primary aliphatic amines* and their salts give red dyes with yellow-green fluorescence of the general formula

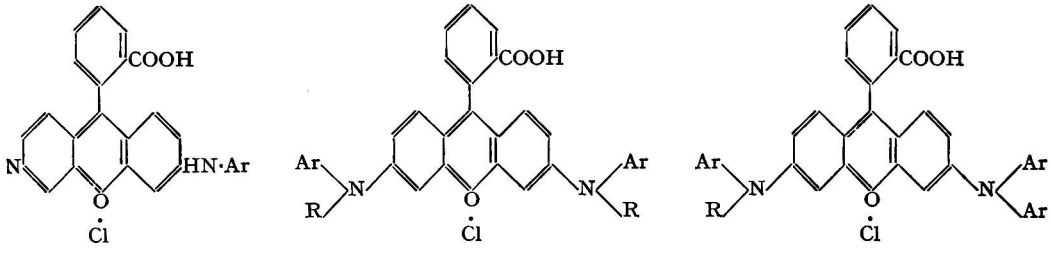


The fluorescence is visible by daylight as well as in ultra-violet light. *Method.*—A drop of the hydrochloric acid test solution is evaporated to dryness in a micro-test-tube or crucible, and the residue is mixed with a small amount of fluorescin chloride (as much as will lie on a knife-point) and double the amount of zinc chloride. The mixture is then heated in an air-bath at 250° to 260° C. until all the

zinc chloride is melted. When cold, the melt is dissolved in 10 per cent. alcoholic hydrochloric acid, and, if the solution shows the fluorescence, a primary aliphatic amine was present. In the presence of only small amounts of amines the solution should be examined in ultra-violet light. For five different amines tested the identification-limit varied from 10γ to 30γ. (ii) *Secondary aliphatic amines* give rhomines with a red colour and orange-red fluorescence of the general formula:



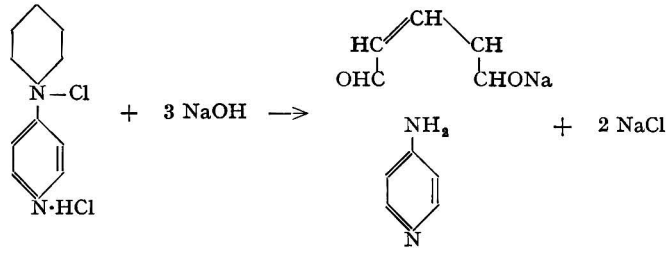
The test is carried out exactly as described before. For diethylamine the identification-limit is 4γ, for piperidine 4γ, and for aceturic acid ester 20γ. (iii) *Aromatic amines* give dyestuffs of the following types according to whether they are primary, or secondary or contain a methyl group:



The alcoholic hydrochloric acid solutions of these dyestuffs are of an intense red-violet colour, but differ from the aliphatic amines in that no fluorescence is shown. The test is carried out as previously described. A table is given of 18 different amines, with the shade of colour and identification-limit (varying from 1γ to 400γ) in each case. (iv) *Acid amides and acid nitriles* react in the test in the same way as primary aliphatic amines. The test solution, however, must not be acid, but neutral, when evaporated to dryness. The fluorescence is yellow. The identification-limit for five different compounds tested varied from 20γ to 50γ. (v) *Pyrrole derivatives* react to form yellow-brown dyestuffs, which show a blue fluorescence in ultra-violet light. The test is carried out as already described, but the test solution should be evaporated in neutral or alkaline solution. Four pyrrole derivatives tested gave identification-limits varying from 12γ to 40γ.

TEST FOR PRIMARY AROMATIC AMINES WITH GLUTACONIC ALDEHYDE.—This is a modification of the "photo-pyridine reaction," Freytag and Neudert (*J. prakt. Chem.*, **1932**, **185**, 15) and Feigl and Anger (*ibid.*, **1934**, **189**, 180). Instead of pyridine, glutaconic aldehyde is used in the test; as this compound will not keep,

the best reagent is 4-pyridyl-pyridinium dichloride, which liberates the aldehyde instantaneously in the presence of alkali.



Method.—Test-paper is impregnated with an alcoholic solution of sodium glutaconic aldehyde enol (prepared by adding 2 *N* alkali to a 1 per cent. dilute alcoholic solution of 4-dipyridyl-pyridinium dichloride) and dried, and a drop of the warm test solution in dilute mineral acid is dropped on to the paper. A red, violet or brown fleck is formed on the paper in the presence of amines, whilst a blank test gives a white fleck on the light brown paper. The test can also be carried out in a micro-crucible, a drop of the test solution, a drop of the 1 per cent. 4-pyridyl-pyridinium dichloride solution, and 2 drops of 2 *N* alkali solution being mixed, and then treated with 3 drops of 2 *N* hydrochloric acid. An intense red to violet colour, or precipitate, indicates the presence of the amine. A table is given of 14 different amines, the colour formed, and identification-limit in each case (0·05γ to 2γ). The reagent is prepared by the method of Koenigs and Greiner (*Ber.*, 1931, **64**, 1049). J. W. M.

Physical Methods, Apparatus, etc.

Conditioning-Box for Cloth Samples. A. W. Bayes. (*J. Text. Inst.*, 1935, **26**, 120–122T.)—The object of the box is to enable samples to be exposed to air at constant humidity before they are tested in the usual strength-testing machines. It should, therefore, be placed as close as possible to these machines, and provision should be made for the rapid removal of single samples without disturbing the humidity conditions in the box. The front of the box, the dimensions of which are 24 × 11·25 in. (height 13 in.), is made of glass, and immediately below the removable lid is an oblong piece of wood which divides the box longtitudinally; it also supports 50 cross pieces (25 on each side), into each of which is set a spring-clip type of clothes peg. Thus, if 5 specimens of warp and weft are taken from each sample, 5 samples may be conditioned together. Under the pegs are two photographic developing dishes containing a saturated solution of common salt and covered with small-mesh wire netting; one (11·75 × 10 × 2 in.) stands on the floor of the box, whilst the other (9·5 × 6·5 × 1·5 in.) is supported on a piece of half-inch board, and the rims are smeared with vaseline to prevent "creeping." The above solution is recommended, since, unlike an unsaturated solution of calcium chloride, it does not change in composition. It is cheaper than magnesium acetate, which has an inconvenient

critical-point at which it changes to a wet cake, and it is more stable than ammonium nitrate. A circulating fan is not required, the humidity being 76 per cent. over the whole range of normal room temperatures, although it is desirable to suspend a paper hygrometer in the box just behind the glass front.

J. G.

Reviews

HANDBUCH DER LEBENSMITTEL-CHEMIE. A. BÖMER, A. JUCKENACK and J. TILLMANS. Vol. VI. FOODSTUFFS CONTAINING ALKALOIDS, SPICES, SALT. Pp. 604. Berlin: Julius Springer. 1934. Price, 76 RM., unbound; 79.60 RM., bound.

This volume treats of coffee, coffee substitutes, tea, maté, kola, cocoa, chocolate, tobacco, spices, and cooking salt, and includes the laws relating to these products. It deals with them with the encyclopaedic thoroughness which has been a feature of the previous volumes of this series, and gives an account of their chemical and microscopical characteristics with a wealth of detail not to be found in any other text-book. The photo-micrographs and drawings are particularly good, and the account both of the chemistry and of the technical production of the various substances is clear and well written. Methods of analysis are given in detail, usually with choice of various processes suited to particular circumstances. The subject-matter is brought right up to date, including references in 1933, but once again we would venture a mild protest against the scarcity of references to English scientific literature; it is annoying to an English reader to find reference to a page in the *Zeitschrift für Lebensmittel* (or other journal), and on turning this up to find that it is an abstract of a paper which appeared, say, in THE ANALYST or the *J.S.C.I.* This happens quite frequently, as, for example, the reference to the well-known paper of Tatlock and Thomson on tea—and could be avoided by giving the original reference to all non-German papers, as well as a reference to German abstracts. The cost of this series of volumes, at least in countries of the sterling bloc, is another serious factor. The present volume is excellent in many ways, and those who desire a really comprehensive treatise on foods will acquire it, but 76 RM. is too high a price for one volume—and that in paper covers.

In view of the work just published by Woodard and Cowland (too recent for inclusion in this volume) (ANALYST, 1935, 135), it is interesting to note the perpetuation of the statement that there is 7 per cent. of tannin in maté, although the authors truly point out that it is a peculiar tannin not precipitable in the ordinary way, as is tea-tannin.

Spices are very well described, and various types, such as capers, not to be found in most books, are included. Pepper in its many varieties is discussed in much detail. It seems at first curiously irrational, yet it is rational, to find salt, the composition of its many varieties, its impurities and methods for its testing, described in a volume devoted to alkaloidal foods and spices. But, in view of its importance in the food factory, its inclusion is justified.

We think this volume maintains the standard of thoroughness and excellence of its predecessors, but we do wish we could persuade its authors, as they wish us to buy it, to pay a little more regard to the convenience of English-speaking chemists. H. E. Cox

ANNUAL REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY, 1934, Vol. XIX. Pp. 836. Published by The Society of Chemical Industry, 46/47, Finsbury Square, E.C.2. Price 12s. 6d. (to members 7s. 6d.).

This valuable annual, which consists of twenty-six reports, including, this year, the biennial report on "Explosives," fully maintains the standard set by its previous issues. The reports are the work of contributors of acknowledged eminence, who, by expert knowledge, wide outlook and considered opinion, have placed the miscellaneous information which the year's work has brought to light in its due relation to what has been established in the past and what may be expected in the future.

From the many subjects of interest to readers of THE ANALYST, space permits of the mention of only a few, but these, which are selected at random, will indicate the helpful nature of this publication.

In the report on "Glass" a resumé of a scheme for the analysis of clays is given. In the "Leather and Glue" report the difficulty of determining the *p*H value of tannery liquors is discussed—a problem by no means confined to these industries. The "Fermentation Industries" report includes a brief account of *r*H values, which are rapidly attaining the same practical importance as *p*H values. The "Iron and Steel" report contains a method for the rapid determination of silicon, based upon the colorimetric molybdate method used for its determination in waters. In the mass of highly interesting matter which forms the "Oils, Fat and Waxes" report will be found a method for the examination of olive oil removed from tinned sardines. The same report deals with such questions as the relation between the development of rancidity and the colour and composition of wrapping materials (a question also dealt with in the "Foods" report), and the factors affecting the vitamin-contents of butter and the fish oils. The "Fine Chemicals, etc.," report contains a summary of the existing knowledge of the chemistry of vitamins B_2 and *C*. The "Sanitation and Water Purification" section mentions the incidence of "mottled teeth" in districts where fluorides occur in the water supply, summarises a method for the estimation of fluorides and discusses the problem of their removal from drinking water (*cf.* ANALYST, 1934, **59**, 378, 380), whilst, from the "Fuel" report we learn that fluorine has been detected in coal in amounts sufficient to cause corrosion in gas-works scrubbers and to render the coal unsuitable for use in glass-bottle manufacture, and it is suggested that the source of the fluorine is infiltrated water.

Much information of absorbing interest is derived from journals familiar only to the specialist, and it is regrettable that a list of the full titles of journals indicated by abbreviated titles in the bibliography has not been included.

The very few misprints which occur lead neither to ambiguity nor to misstatement, and their corrected forms are obvious; consequently, they do not

require enumeration. In the first line on p. 214 the word "peroxide," which should follow the word "sodium," has been omitted. The volume contains a name-index and an efficient, though not exhaustive, subject-index.

A prominent feature of the whole work is the easy narrative style adopted by each contributor, which makes this work not only a thoroughly competent, but also a genial and companionable guide for all those whose duty or pleasure it is to roam through the recent literature of Applied Chemistry.

A. O. JONES

THE SCIENCE OF RUBBER. By Prof. K. MEMMLER and Co-WORKERS. Authorised English Translation. Edited by R. F. DUNBROOK and V. N. MORRIS, in collaboration with the Research Staff of the Firestone Rubber Company (U.S.A.). Pp. 675, Bibliography and Indexes. New York: Reinhold Publishing Corporation. 1934. Price $15.00.

Memmler's *Handbuch der Kautschuk-Wissenschaft* was reviewed in THE ANALYST for January, 1931 (p. 71), and this authorised English translation follows closely the original German text. Several improvements have to be noted, however, not least of which is the valuable leavening influence of the American translators, who have brought the text up to date and inserted numerous references to the English and American literature. The addition of an extensive bibliography adds greatly to the value of the book for reference purposes, and author- and subject-indexes are provided.

As is to be expected with a composite work of this character, where separate sections are contributed by different individuals, the method of treatment differs somewhat from section to section, and this detracts a little from the readability of the book. The book unavoidably suffers in the same sense from the fact of translation, however well done.

The chapters or sections are not lettered and numbered as in the original German edition, but follow the same order, *viz.* Introduction; Botany, Cultivation, Collection and Preparation of Rubber; The Chemistry of Rubber; The Vulcanisation of Rubber; Chemical-Analytical Testing Methods; Physics of Rubber; Physical Testing Methods; and Microscopy of Technical Vulcanisates.

It is obviously not possible to read the whole of such an extensive book for review purposes, but a large number of tests have been made for reference purposes, and the treatise has come out with flying colours. For this reason, alone, it is likely to be found on the shelves of all rubber technologists.

A few small points noted by the reviewer may be mentioned. The illustration of Hevea particles on p. 54, which appeared in the German edition, will certainly strike most workers with latex as unusual, and one wonders how such a picture was obtained. In the botanical and plantation section fuller reference (with illustrations) should be made in future editions to the scientific aspects of the preservation and centrifugal concentration of latex for manufacturing purposes, which is only discussed briefly (p. 87). In the extensive section on the theory of vulcanisation (still the rubber chemist's most thorny problem) the translators, in inserting a note on the "reinforcement theory" of vulcanisation (p. 299, footnote), have missed the reference to the original contribution on this subject

(*Fourth Report on Colloid Chemistry*, 1921–22, p. 366; also *cf. J.S.C.I.*, 1928, **47**, 37T, and 1929, **48**, 60T), and might, perhaps, repair the omission in future editions.

The printing and paper of this book are excellent, although the cover, perhaps, is not attractive to English eyes; the price is adequate. W. H. STEVENS

METHODIK DER VITAMINFORSCHUNG. C. BOMSKOV, Ph.D. Pp. xvi+301. Leipzig: Georg Thieme. 1935. Price M. 24.

This is a very full account of the methods used by workers in different countries for making qualitative tests for vitamins. A little consideration has also been given to the quantitative estimation of these factors. Such details as the constitution of diets, duration of experimental periods and, in some instances, examples of results actually obtained, have been carefully quoted. Short accounts are given of the chemistry of the better-known vitamins, and reports of those vitamins whose existence is yet only suspected.

It is, however, to be regretted that so little attention has been given to the quantitative methods of estimation. The International Standards for the vitamins *A*, B_1, *C* and *D* are described in their respective sections, but there is no guide as to how the Standards should be used. An account of the general principles of biological methods of estimation would have been invaluable in this book. In particular, it might have been pointed out that it is absolutely essential to make a simultaneous test of the standard with every estimation which may be made of the vitamin-content of a substance. A closer search of the literature would have revealed the necessity for this procedure, and a realisation of its importance would have led the author to explain why such terms as the rat-growth unit, and the guinea-pig unit should *not* be used, and how impossible it is to convert any one of those units satisfactorily into International Units. The author, however, has not been critical; he has faithfully reproduced his findings in so far as his search has carried him.

The book is well printed and the illustrations are clearly reproduced.

K. H. COWARD

TABLE OF INCOMPATIBLES. R. L. WORRALL. London: John Bale, Sons & Danielson. Price 1s. 6d. net.

The Table of Incompatibles is printed on a sheet of good quality paper, approximately 17 inches by 15½ inches. It is intended for prescribers, and on one side are lists of oxidising and reducing substances, and acid and alkaline preparations which must not be prescribed together. On this side there are also lists of substances which should be prescribed alone, of those which may cause explosions, of those which decompose, and of those which deliquesce. On the reverse side of the paper 56 substances or groups of substances are depicted graphically on all four sides of a square. Black dots at intersecting lines indicate incompatibility, and open circles the possibility of incompatibility. The interest for the analyst lies in the fact that when a medicine is presented for analysis, any possibility of change in the ingredients due to interaction or decomposition, can, for most common substances, be readily detected, and the analytical procedure can be modified accordingly from the outset. S. G. STEVENSON