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 4th, the President, Mr. John Evans, F.I.C., being in the chair.

Certificates were read in favour of:—Frederick Frank Beach, M.A., B.Sc., F.I.C., Thomas Gifford Elliot, F.I.C., Frederick John Flowerdew, B.Sc., A.I.C., M.P.S., John Arthur Heald, M.C., B.Sc., F.I.C., Francis Edwin Needs, F.I.C., and Derrick John Saxby, B.Sc., A.I.C.

The following were elected members of the Society:—Ronald Andrew Balding, Bertram Eastwood Dixon, M.Sc., A.I.C., A.C.G.F.C., Arthur Glover, M.Sc., A.I.C., Ralph Gordon Harry, A.I.C., Reginald Milton, B.Sc., Roy Warren Watridge, B.Sc., F.I.C.

The following papers were read and discussed:—"The Determination of Small Quantities of Fluorides in Water," by Guy Barr, B.A., D.Sc., and A. L. Thorogood, B.Sc.; "A Test for Ethylene Glycol and its Application in the Presence of Glycerol," by A. W. Middleton, B.Sc., A.I.C.; and "The Detection of Diamines in Leather," by W. Mather, F.I.C., and W. J. Shanks.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Manchester on April 14th, 1934. The Chairman (Prof. W. H. Roberts) presided over an attendance of thirty-five.

The Chairman, on his own behalf and that of the members, congratulated Mr. J. Evans on his election as President of the Society.

The following papers were read and discussed:—"The Micro-Determination of the Molecular Weight of Volatile Liquid Compounds," by A. F. Colson, B.Sc., A.I.C.; "Note on the Determination of Chromium in the Presence of Iron, Aluminium and Phosphoric Acid," by J. Haslam, M.Sc., A.I.C., and W. Murray; "The Composition and Freezing-point of Colostrum," communicated by G. D. Elsdon, B.Sc., F.I.C.; and "The Technique of the Freezing-point Test for Milk," by G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

Standards for Jam

THE Council has considered a letter received from the Food Manufacturers' Federation (Incorporated), relating to two matters connected with the standards and definitions for jam agreed upon by the Society and the Federation (ANALYST, 1930, **55**, 694).

(i) The Committee of the Federation, having given consideration to the fact that certain members of the Federation have found it difficult to comply with the regulation in regard to size of type for the labelling of lower fruit standard jams, decided to suggest for the consideration of the Society that, in place of the present requirement, that the words "with other fruit juice" must be in letters of size equal to that of the name of the fruit or fruits, it should be permitted to use type of not less than half the size of that of the fruit name, with a minimum height of one-eighth inch. The minimum would apply in cases where the fruit name was printed in letters of quarter of an inch or less in height.

Examples: Strawberry (1 inch high)
With other fruit juice ($\frac{1}{2}$ inch high)
Strawberry ($\frac{1}{4}$ inch high)
With other fruit juice ($\frac{1}{8}$ inch high).

In addition, of course, the label must bear the lower fruit standard as provided for in the regulations.

(ii) The Committee ruled that jams sold as "blackberry with apple jelly" should in future be described on the label as "blackberry and apple," and conform to the full fruit standard.

The Council of the Society has agreed to these alterations in the agreement.

Notes on a Semi-Quantitative Modification of the Elaidin Test

BY H. N. GRIFFITHS, PH.D., AND T. P. HILDITCH, D.SC., F.I.C.

(*Read at the Meeting of the North of England Section, February* 10, 1934)

THE well-known elaidin test, as first proposed by Poutet in 1819, for discriminating between non-drying and drying oils, consisted in shaking the fatty oil for three minutes with prescribed proportions of mercury and nitric acid, after which it was set aside for twenty minutes, and then again shaken for one minute. The relative hardness of the final product, and the time taken for this consistency to be attained, were observed and compared with the behaviour of various known oils under the same conditions of test. Various modifications of the test were proposed from time to time, and Archbutt (*J. Soc. Chem. Ind.*, 1886, **5**, 303), after reviewing these suggestions, recommended the addition to the fatty oil (96 grms.) of a reagent (8 grms.) prepared by dissolving mercury (18 grms.) in nitric acid (15·6 ml.)

of sp.gr. 1·42; the mixture was placed in a wide-necked stoppered bottle immersed in water at about 25° C., and was shaken at intervals of ten minutes until solidification occurred. The length of time required for the fat to acquire a solid consistency, and the degree of solidity attained, were recorded by Archbutt for various oils. Non-drying oils, such as olive and almond oils, gave hard solid fats in two or three hours; mustard, neat's foot, and sometimes rape oil, gave butter-like products, and semi-drying oils, such as cotton-seed or sunflower-seed oils, were also observed to give products of a buttery or pasty texture; but linseed, hemp, walnut, and other drying oils remained quite liquid under the conditions of the test. Archbutt also records observations on the results obtained when the test was applied to olive oil mixed with certain other oils, from which it appears that he was able to detect the presence of 10 per cent. of rape or cotton-seed oil in olive oil from the consistence of the isomerised product and the time occupied in reaching the final consistence; poppy-seed oil had a marked effect, and could probably be detected in olive oil in proportions as low as 5 per cent., but the presence of 20 per cent. of "best nut oil" (? ground-nut oil) had little influence beyond somewhat prolonging the time taken to reach the final consistence, which was not quite so pronounced as in the case of the genuine olive oil.

We have lately been occupied with a quantitative investigation of the oleic-elaidic acid equilibrium and with an attempt to utilise this balanced reaction in the estimation of triolein in natural fats (*J. Chem. Soc.*, 1932, 2315). Although we were unable to achieve the latter object (owing to the low yield—30 per cent.—of trielaidin from triolein), we found that trielaidin could be separated from triolein by crystallisation from acetone under defined conditions; and that, consequently, within certain limits, a quantitative character could be given to the elaidin test as applied to fatty oils. Owing to changes in the nature of the oils used to adulterate olive oil, and to the development of improved alternative analytical procedures, the elaidin test is probably now of much less interest to the analyst than formerly. Nevertheless, it may be useful to record the proportions and characteristics of the crystallised "elaidins" obtained from a variety of oils under the standardised conditions which we are about to describe.

Isomerisation of a Fatty Oil by the Poutet Reagent.—We prefer to introduce the requisite quantities of mercury and nitric acid (sp.gr. 1·42) into the oil under examination, instead of preparing a stock solution of the reagent, as recommended by Archbutt.

The fatty oil (10 to 20 grms.), from which free fatty acids should be almost or entirely absent, is shaken with mercury (0·2 to 0·4 grm.) and nitric acid (0·5 to 1·0 ml.) in a stoppered bottle immersed in water at room temperature for one hour, and then left to stand overnight. The product, in solution in ether, is washed with dilute nitric acid to remove mercury compounds, and then with water until free from nitric acid. Ether and moisture are subsequently removed by evaporation, the residue being finally heated in a vacuum at 95° C. for a short time.

Isolation of Crystalline Glycerides from the Isomerised Oil.—The dried product (5 grms.) is crystallised from acetone (20 ml.), the solution being

kept at room temperature overnight and finally cooled at 0° C. for two hours. The separated crystals are collected and washed four times with acetone (5 ml. each time), dried in a vacuum desiccator, and weighed. The m.pt., iodine value and saponification value of the separated crystals are then determined.

Before describing the results obtained with various fatty oils, we may quote data which illustrate the application of the method to pure triolein and trielaidin.

DETERMINATION BY THE ABOVE PROCEDURE OF TRIELAIDIN IN MIXTURES CONTAINING KNOWN PROPORTIONS OF TRIOLEIN AND TRIELAIDIN.—Mixtures were made with synthesised triolein (iodine value 85·2) and synthesised trielaidin (m.pt. 42·8° C., iodine value 85·2, solubility in acetone at 0° C., 0·29 grm. in 100 ml.) in various proportions; these were submitted to crystallisation from acetone as described above, with the following results:

TABLE I

Trielaidin present, per cent.		100·0	78·6	61·2	39·4	19·6
Trielaidin isolated	per cent.	99·3	78·4	61·0	39·2	18·3
	m.pt., ° C.	42·3	42·1	42·2	42·0	42·3

ISOMERISATION OF SYNTHESISED TRIOLEIN.—The results of three typical experiments are given in the next table; crystallisation of the trielaidin was carried out, in each case, on 5 grms. of the isomerised glycerides.

TABLE II

Triolein used Grms.	Crystallised glycerides from acetone			Trielaidin Per Cent.
	Per Cent.	M.pt. ° C.	Iodine value	
18·0	32·6	40·5	81·4	31·1
9·4	26·7	40·5	82·9	26·3
8·8	28·5	41·5	83·4	28·0

The m.pt. of the crystallised product, which in each case was but little below that of trielaidin, was raised somewhat on admixture with the latter compound. We conclude, therefore, that di-elaido-mono-oleins do not separate under the conditions employed. The slight depression in m.pt., and the slightly low iodine values, are readily accounted for by the presence of traces of nitrogenous addition products which, as we have pointed out elsewhere (*loc. cit.*), are produced during the process of isomerisation.

APPLICATION OF THE PROCEDURE TO FATTY OILS.—We obtained, with a number of oils, the results summarised in Table III.

INTERPRETATION OF THE ANALYTICAL DATA.—It is essential to bear in mind, in considering the above figures, that the natural glycerides in vegetable fats are so built up that they contain, in general, minimum proportions of simple triglycerides. Hence an oil, such as olive or ground-nut oil, which was formerly supposed to consist very largely of triolein, is really made up of mixed glycerides in which, roughly speaking, one radical of acids present in much less amount than oleic acid (*e.g.* palmitic or linoleic acid) is linked with two oleic radicals in the glyceride molecule, and only the excess, so to speak, of oleic acid appears as

simple triolein. Consequently, the "elaidins" do not consist, as would formerly have been supposed, of trielaidin, but of a mixture of the latter with the mono-saturated-dielaidins produced by isomerisation of some of the mono-saturated-dioleins originally present. Inspection of the iodine values of the crystallised "elaidins," given in the preceding table, illustrates this feature at once; the iodine value of the products is in all cases much lower than that of trielaidin (86·2).

TABLE III

Oil	Iodine value	Appearance of the elaidinised product	"Elaidins" crystallised from acetone			
			Per Cent.	M.pt. °C	Iod. val.	Sap. val.
Olive	84·9	Hard, solid mass	33·1	33·5	67·1	197·0
			35·5	37·0	68·8	196·1
Tea-seed	86·3	,, ,, ,,	38·8	36–37	73·0	193·2
			35·5	37–38	73·9	193·0
Almond	96·5	,, ,, ,,	29·3	39	79·5	191·3
			26·8	38·5	78·5	191·5
Ground-nut	90·5	Pasty mass	32·9	33	68·8	189·4
			31·8	35	65·9	189·9
Rape-seed	102·9	Butter-like mass	7·6	32	79·8	—
			7·9	32	79·3	184·0
Mustard-seed	104·0	,, ,, ,,	3·6	33	71·0	—
Cotton-seed	103·0	Semi-solid	1·3	—	45·4	—
			2·1	—	50·2	—
Soya-bean	129·6	Red liquid	Nil	—	—	—
Rubber-seed	136·2	,, ,,	Trace	—	—	—
Hemp-seed	166·3	,, ,,	Nil	—	—	—
Linseed	182·6	,, ,,	Nil	—	—	—

The mixed fatty acids of each oil submitted to the elaidin reaction during this work consisted of saturated, oleic, linoleic, linolenic, and erucic acids in the proportions given in Table IV. These data were obtained by the ester-fractionation method of analysis, supplemented (when linolenic acid was present) by thiocyanometric analysis; results by the latter process were also confirmed by estimation of oleic acid in the mixed fatty acids by means of the oleic-elaidic transformation, according to a procedure which we have recently described (*J. Soc. Chem. Ind.*, 1934, **53**, 75 T; ANALYST, 1934, 363). In Table IV the individual percentages of palmitic and other saturated acids have been omitted, since, for the purpose of the present discussion, the total proportion of saturated acids suffices.

It may be pointed out that, with the exception of olive oil (which contains 2 per cent. of tripalmitin; *cf.* Hilditch and Jones, *J. Chem. Soc.*, 1932, 805), none of the oils examined contains any appreciable quantity of fully-saturated glycerides.

Olive, tea-seed and almond oils are the only instances, in the groups studied, in which it is likely that any substantial amount of triolein is present. In these oils, also, the ratio of saturated to unsaturated acids is sufficiently low to justify the supposition (in view of the present knowledge of glyceride structure in vegetable

fats) that nearly all the saturated acids are combined in the form of mono-saturated-di-unsaturated glycerides. Further, since their contents of linoleic acid are relatively small, and since palmitic acid predominates in their saturated acids, the crystallised "elaidins" are probably made up almost wholly of mono-palmito-di-elaidins and tri-elaidin (with respective iodine values 59·2 and 86·2). If this is the case, the composition of the elaidins could be calculated approximately from their observed iodine values; but, unfortunately, our experience with trielaidin, isolated from pure triolein by the same procedure, shows that the iodine value of the product is usually somewhat low (82 to 83), and any estimate based on the observed iodine values would, therefore, be somewhat untrustworthy. The data for these three oils indicate, however, that something approaching half of the saturated acids present in the original fats has, in each case, been isolated in the form of mono-saturated-di-elaidins.

TABLE IV

	Percentage of mixed fatty acids				
	Saturated	Oleic	Linoleic	Linolenic	Erucic
Olive	12·7	79·8	7·5	—	—
Tea-seed	9·3	83·3	7·4	—	—
Almond	5·6	77·0	17·4	—	—
Ground-nut	17·7	60·4	21·9	—	—
Rape-seed	2	32	15	1	50
Mustard-seed	4	24·5	19·5	2	50
Cotton-seed	25·1	29·6	45·3	—	—
Soya-bean	13·4	26·1	54·7	5·8	—
Rubber-seed	18·4	23·6	43·3	14·7	—
Hemp-seed	8·6	6·7	68·8	15·9	—
Linseed	9·7	9·6	42·6	38·1	—

The case of ground-nut oil is complicated by the presence, on the one hand, of a higher relative proportion (22 per cent.) of linoleic acid in the mixed acids and, on the other, by that of saturated acids, in addition to palmitic acid, containing 18, 20, 22, and 24 carbon atoms in the molecule. Since ground-nut oil contains only about 60 per cent. of oleic acid, we are inclined to doubt, in view of the results with other oils, the presence of much triolein in the glycerides. Although the yield and iodine value of the ground-nut "elaidin" are not very different from those of olive or tea-seed "elaidins," we incline to believe that it does not represent the same type of material, but may be more complex in character and include, for example, glycerides containing arachidic and linoleic, in addition to elaidic acid. This is borne out, to some extent, by the marked difference in consistency between elaidinised ground-nut oil and elaidinised olive, tea-seed or almond oils. We hope, at a later date, to prepare elaidins from these four oils in sufficient quantity to permit us to make a more detailed study of their component acids.

Cotton-seed oil is interesting because the small quantity of elaidins produced has a relatively low iodine value. Here oleic acid forms only about 30 per cent. of the mixed acids, whilst the saturated acids (chiefly palmitic) amount to almost as great a proportion (25 per cent.). Triolein is almost certainly completely absent, and the low yield of elaidins evidently consists mainly of palmito-di-elaidin (iodine

value 59·2), which is, however, accompanied by a certain amount of dipalmito-elaidin (iodine value 30·5).

Oils of the rape and mustard group also yield only small quantities of crystallised "elaidins"; from the very low contents (2 to 4 per cent.) of saturated acids in the original mixed acids, and the iodine and saponification values of the "elaidin," it would seem that the latter consists mainly, in this case, of mixed elaido-brassidins. It is, of course, possible, though *a priori* distinctly less likely, that the products are mixtures of trielaidin and tribrassidin.

Finally, in the four "drying" oils, oleic acid is definitely low in proportion to the remaining acids, and forms only from 6·7 to 26·1 per cent. of the mixed acids. No solid elaidins separate on isomerisation (except for a trace from rubber-seed oil, the acids of which contained 18·4 per cent. of saturated acids as well as 23·6 per cent. of oleic acid), and triolein is evidently not present; indeed, the oleic acid is almost certainly distributed in the glyceride molecules, so that, substantially, only mono-oleo-compounds occur in these oils (*cf.* for linseed oil, Eibner, Widenmayer and Schild, *Chem. Umschau*, 1927, **34**, 312).

UTILITY OF THE ELAIDIN REACTION IN DETECTING ADULTERATION OF OLIVE OIL.—Since the chief analytical interest of the elaidin test lies in its possible application in the examination of olive oils, it may be well to consider how far the amended procedure suggested in this paper is likely to be of assistance in this direction. It does not appear very serviceable, at the outset, in the detection of tea-seed oil in admixture with olive oil, although the crystallised elaidin of tea-seed oil has a definitely higher iodine value and slightly lower saponification value than that from olive oil; the differences are not sufficient, however, to permit of the method being employed with much success in this instance. It is remarkable how closely olive and tea-seed oils resemble each other in their fatty-acid composition and also in their glyceride structure; the only significant difference is that the fruit-flesh olive oil contains a very small proportion (2 per cent.) of tripalmitin. This feature, although evident as a result of complete oxidation of large quantities of oil, does not lend itself to use as an analytical means of identification. Apparently, differentiation between the two oils must be sought in the characteristics of their non-fatty components—for example, the iodine values of the unsaponifiable matter (Bolton and Williams, ANALYST, 1930, **55**, 5).

Almond oil, in consequence of its low saturated acid content, yields an elaidin which resembles trielaidin in iodine and saponification values more nearly than that of either olive or tea-seed oil; in consequence, the proportion of elaidin from almond oil is several per cent. lower than in the latter two oils, whilst its melting-point is definitely higher (38 to 39°). The yield of elaidin from ground-nut oil is intermediate between those of the products from olive and almond oil, and its iodine value is little different from that of olive-oil elaidin, but its saponification value is definitely lower (189 to 190, as compared with 196 to 197), its m.pt. is somewhat lower, and its consistence is less brittle.

The proportions of elaidins produced from the remaining oils (*cf.* Table III) are small or negligible, so that the presence of these oils in any quantity in a reputed olive oil would be clearly indicated by a pronounced decline in the total yield of crystallised elaidins. In these circumstances, also (except in presence of added

rape or mustard-seed, and possibly cotton-seed, oils), the m.pt., iodine and saponification values observed would be those of the olive oil elaidin. Rape and mustard-seed oil would be expected, in addition to causing a decreased yield of elaidin, to have a depressant effect on its melting-point, the iodine value of which would be somewhat increased, whilst its saponification value would be low in comparison with the corresponding figures for olive oil elaidin. Cotton-seed oil, if present in some quantity, would cause a fall in both the yield and the iodine value of the crystallised elaidin.

Deviations from the average values of the crystallised olive oil elaidin in the directions indicated in Table V might be accepted as indications of the probable presence, in a specimen of olive oil, of other oils as follows:

TABLE V

"Elaidins" crystallised from acetone				Oil suspected
Yield (on oil) Per Cent.	M.pt. °C.	Iod. value	Sap. value	
33–35	34–37	67–69	196–197	(Genuine olive oil).
Same	36–38	Slightly higher	Slightly lower	(?) Tea-seed.
Lower, but not less than 30 per cent.	Not lower	Somewhat higher	Between 196 and 190	Almond (possibly rape or mustard in small proportions).
„ „ „	Somewhat lower	As for olive	Lower than for olive	Ground-nut.
„ „ „	As for olive	As for olive	As for olive	Semi-drying or drying oils (up to about 20 per cent. of the original oil).
Below 30 per cent.	Somewhat lower	Higher	Low	Rape, mustard-seed (over 20 per cent. of the original oil).
„ „ „	As for olive	As for olive	As for olive	Semi-drying (*e.g.* cotton-seed) or drying oils (over 20 per cent. of the original oil).

We desire to thank Messrs. Lever Brothers, Ltd., whose Research Studentship in this laboratory was held by one of us (H. N. G.) during the course of this work.

THE UNIVERSITY
LIVERPOOL

Quantitative Determination of Acetone and Ethyl, Butyl and Iso-Propyl Alcohols in Fermentation Liquors

G. L. STAHLY, O. L. OSBURN AND C. H. WERKMAN

THE differential distribution of the fatty acids between two immiscible solvents is employed in the partition method described by Werkman (*Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 302) for the quantitative determination of the acids in a mixture. The partition method is adapted in the present communication to the quantitative determination of mixtures of acetone and ethyl, butyl and iso-propyl alcohols, or any combination of these. A need for such a method is felt in investigations involving the butyl-acetonic fermentation.

In the present procedure a neutral or slightly alkaline aliquot portion of the fermentation liquor is distilled directly. Acetone is determined in an aliquot part of the distillate by a modification of Messinger's method, as described by Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39). The alcohols are then oxidised in a second aliquot part of the distillate without removing the acetone. Ethyl alcohol is oxidised to acetic acid, whilst 89·6 per cent. of the butyl alcohol is oxidised to butyric acid and 10·4 per cent. to acetic acid. These values agree with those obtained by van der Lek (*Onderzoekingen over de Butyl-Alkoholgisting*, Thesis, Delft, 1930) and Werkman and Osburn (*Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 387). It was found that 94 per cent. of the iso-propyl alcohol is oxidised to acetone. The oxidised mixture, containing butyric and acetic acids and acetone, is distilled. The acetone in the distillate is determined iodimetrically, and the acids are determined by the partition method. By a simple calculation of the partition coefficient, the percentages of ethyl and butyl alcohols can be read directly from a nomogram (Fig. 3).

Van der Lek, working with similar mixtures, determined acetone by precipitation with 2, 4-dinitrophenyl hydrazine. The alcohols were oxidised with potassium dichromate and sulphuric acid at two different temperatures. The acids were steam-distilled and quantitatively determined by the method of Duclaux. The iso-propyl alcohol was oxidised to acetone and determined in the same manner as the acetone in the original mixture. Van der Lek's method requires considerably more time than the method described in this paper.

Adams and Nicholls (ANALYST, 1929, **54**, 2) quantitatively analysed mixtures of acetone, ethyl alcohol, and iso-propyl alcohol. They oxidised the mixture with potassium dichromate and sulphuric acid at room temperature. The acetone and acetic acid resulting were steam distilled, the acid was titrated, and the acetone was distilled and determined by specific gravity or colorimetrically.

PROCEDURE.—The procedure we have followed is outlined in Fig. 1. The alcohols and acetone are distilled from 500 ml. of the neutral or slightly alkaline fermentation liquor by direct distillation. If the mixture froths much, distillation

can be carried out from slightly acid solution; about 250 ml. of the distillate thus collected are neutralised and re-distilled. The second distillate is brought to a volume of 200 ml. and 50 ml. of it are placed in a 200-ml. balloon flask containing 10 grms. of potassium dichromate and 25 ml. of 85 per cent. orthophosphoric acid. The flask is connected at once with an efficient reflux condenser and crushed ice is placed in the upper portion of the condenser tube. A few glass beads or pieces of

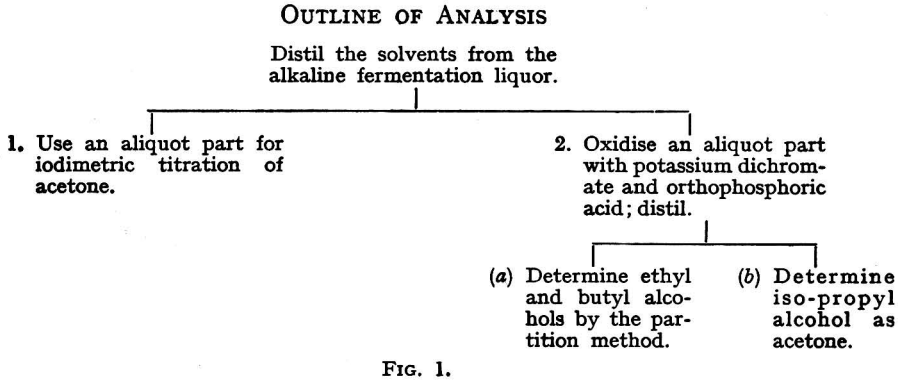

FIG. 1.

porcelain are used to prevent bumping. The mixture is heated so that boiling starts after two minutes, and gentle boiling is continued for six minutes. During the heating the condenser tube is rinsed once or twice with small portions of carbon dioxide-free water. The flask, with the condenser still attached, is then cooled rapidly by immersing in cold water. The condenser tube is again rinsed into the flask. The latter is removed, and quickly connected with a Liebig condenser, and the mixture is distilled into an iced receiver. The outlet tube leading from the flask to the condenser should be of fairly large bore, to prevent any liquid from being mechanically forced over into the distillate. There is no tendency to bump and the distillation proceeds smoothly. Frothing, which occurs near the end of the process, is maintained for two or three minutes until the froth nearly, but not quite, fills the flask. All the acetone and organic acids are distilled. Phosphoric acid has not been found to distil over in significant quantities. As soon as the foam has subsided, the distillation flask is removed and the stopper and end of the outlet tube are rinsed to remove any oxidising reagents. The condenser tube is then rinsed, and the water is collected in the receiver containing the distillate, which should be colourless. The volume is made up to 200 ml. with carbon dioxide-free water, and aliquot portions are taken for the different analyses, the determinations being carried out as follows:—

DETERMINATION OF ACETONE.—Acetone is determined quantitatively in an aliquot part of the distillate by a modification of Messinger's method, as described by Goodwin (*J. Amer. Chem. Soc.*, 1920, **42**, 39) (Fig. 1).

A temperature of approximately 0° C. is maintained, and the iodine is allowed to react for 10 minutes before acid is added and the iodine back-titrated. Under these conditions the acetone reacts completely with the iodine, whereas the ethyl and iso-propyl alcohols do not react. Table I gives the results of typical analyses.

TABLE I

QUANTITATIVE DETERMINATION OF ACETONE

Mixture	Contained ml.	Acetone found ml.		
1. Acetone	1·30	1·31	1·30	1·30
2. Acetone	1·30	1·30	1·29	
Ethyl alcohol	2·50			
3. Acetone	1·235	1·235	1·235	
Iso-propyl alcohol	2·50			

All solutions are one-tenth molar.

DETERMINATION OF ISO-PROPYL ALCOHOL.—Iso-propyl alcohol is oxidised to acetone and determined iodimetrically in the distillate. In a series of trials with iso-propyl alcohol alone the following percentages were recovered as acetone:—95·3, 94·7, 93·6, 92·8, 93·0, an average recovery of 93·9 per cent. Iso-propyl alcohol in mixtures with butyl and ethyl alcohols gave substantially the same results. Likewise, when acetone alone was subjected to routine oxidation and distillation, 94 per cent. was recovered. These results indicate that the loss of 6 per cent. occurs after the iso-propyl alcohol has been oxidised to acetone. To find the quantity of iso-propyl alcohol, therefore, divide the total acetone after oxidation by 0·94, and subtract the acetone present in the original sample.

Neither mixtures of iso-propyl and butyl alcohols, nor those of acetone and butyl alcohols gave higher yields of acetic acid than did butyl alcohol alone, so that failure to recover 100 per cent. of the acetone is apparently not due to oxidation to acetic acid.

DETERMINATION OF ETHYL AND BUTYL ALCOHOLS.—Sixty ml. of the distillate, which should be approximately 0·03 *N* acid, are shaken vigorously for one minute in a separating funnel with 25 ml. of acid-free anhydrous diethyl ether at 25° C. After three minutes 50 ml. of the aqueous phase are withdrawn and titrated with standard sodium hydroxide solution, phenolphthalein being used as indicator. The number of ml. of sodium hydroxide solution required is recorded as P'. Fifty ml. of the unpartitioned distillate are titrated, and the number of ml. required is recorded as M. Then $P'/M \times 100 = K$. This value, K, is designated the percentage partition constant for the acid solution.

In Fig. 2, the values of K are plotted against the percentages of acetic and butyric acids. The graph was drawn by finding the values of K, as just explained, for various known mixtures of pure acetic and butyric acids. Therefore, after K has been computed for any mixture of acetic and butyric acids, the percentage composition on a molar basis can be read directly from the graph. The partition constant for pure acetic acid is 83·3; that for pure butyric acid 34·5.

In order to convert K into percentage of ethyl and butyl alcohol, it is first necessary to determine the behaviour of these alcohols under our conditions of oxidative treatment. Ethyl alcohol, after oxidation, gave the same value for K as did pure acetic acid, indicating acetic acid to be the only acid produced. Butyl alcohol gave a mixture of butyric and acetic acids. Under the conditions of

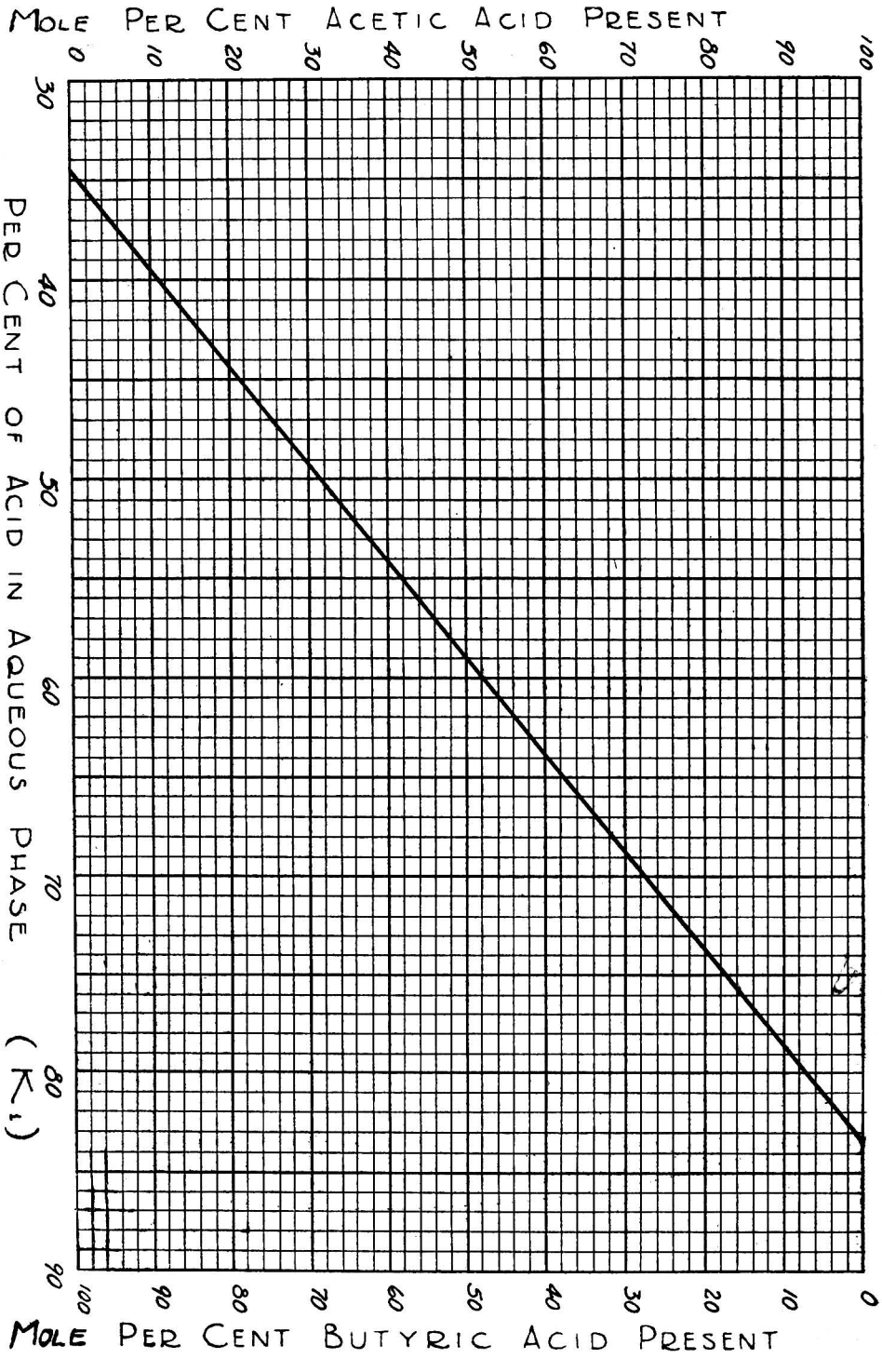
Mole Per Cent Acetic Acid Present
0 10 20 30 40 50 60 70 80 90 100
30 40 50 60 70 80 90
Per Cent of Acid in Aqueous Phase (K1)
100 90 80 70 60 50 40 30 20 10 0
Mole Per Cent Butyric Acid Present

Fig. 2.

oxidation used in these tests, an average of 89·6 per cent. of butyric acid was produced. In order to arrive at this value for butyric acid, solutions of butyl alcohol were oxidised, and their partition constants were computed. By using these constants in Fig. 2 the percentages of butyric acid can be read directly. The values obtained were: 89·8, 89·0, 90·0, 89·6, and 89·6 per cent. of butyric acid. No formic or propionic acid could be detected. The average percentage of the butyl alcohol recovered as acids was 98·2 per cent., assuming that one mole of alcohol yields one mole of acids.

It is convenient to construct a diagram from which the percentage of each alcohol may be read directly. This is done by determining the partition constants for the oxidised products of pure butyl alcohol (39·2) and ethyl alcohol (83·3) and various known mixtures of them. These values of K are plotted in Fig. 3 against the molar percentages of the alcohols.

An example will make clear the use of Fig. 3. An unknown mixture of ethyl and butyl alcohols, after oxidation, gave a partition constant of 60. From Fig. 3 it is seen that if K = 60, the alcohols in the mixture must be 47·0 mole per cent. of ethyl alcohol and 53·0 mole per cent. of butyl alcohol. From the amount of total acids present the concentrations of each alcohol in the mixture can be readily computed.

The partition constant obtained with mixtures of acetic and butyric acids was not affected by the presence of acetone in the concentrations used in these experiments.

Results obtained by using these methods on known mixtures of acetone and the alcohols are recorded in Table II. Compounds of a high degree of purity were twice distilled, and the middle fraction of constant boiling-point was used. All volumes are expressed as ml. of 0·1 molar solutions.

TABLE II

QUANTITATIVE DETERMINATION OF MIXTURES OF ACETONE AND ALCOHOLS

Mixture	Contained ml.	Found ml.	Per cent. of original found
1. Acetone	13·0	13·12	101·0
Iso-propyl alcohol	50·0	49·8	99·6
Ethyl alcohol	50·0	49·0	98·0
Butyl alcohol	100·0	99·5	99·5
2. Acetone	10·4	10·49	100·8
Iso-propyl alcohol	40·0	41·1	102·7
Ethyl alcohol	18·8	18·3	97·2
Butyl alcohol	100·0	101·3	101·3
3. Ethyl alcohol	50·0	50·9	101·8
Butyl alcohol	200·0	191·5	96·0

All solutions are one-tenth molar.

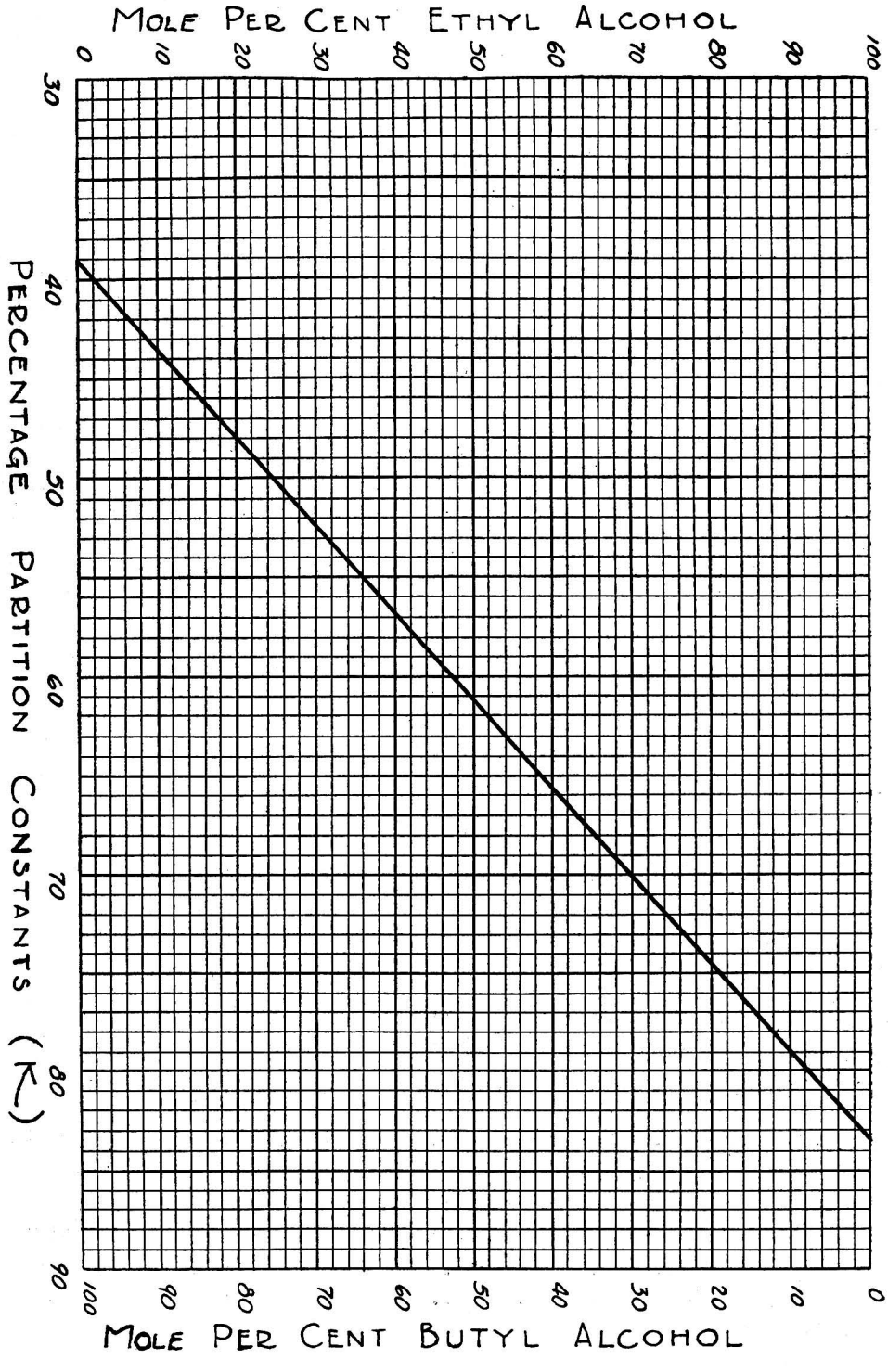
MOLE PER CENT ETHYL ALCOHOL
0 10 20 30 40 50 60 70 80 90 100
PERCENTAGE PARTITION CONSTANTS (K)
30 40 50 60 70 80 90
100 90 80 70 60 50 40 30 20 10 0
MOLE PER CENT BUTYL ALCOHOL

Fig. 3.

DISCUSSION.—The procedure outlined should be followed in detail. The concentration of the phosphoric acid should be constant, since any change causes a small shift in the ratio of acetic to butyric acid originating from the butyl alcohol. The manner of heating the mixture may also cause variation in the acid ratio. Care must be taken to prevent loss of the more volatile compounds during each stage of the heating process. Likewise, the condensers must be well rinsed with water free from carbon dioxide at the close of each process. The temperature of the partition mixture should not vary by more than $\pm 2°$ from 25° C. The ether used must be anhydrous and free from acids.

The method here described is accurate for solutions which contain from 0·02 to 0·05 *N* acid after oxidation. The partition constants for the acids shift slightly as the acid solutions vary in concentration. If it is necessary to work with other concentrations, new constants should be established to fit the conditions.

The method of analysis outlined in this paper is accurate, convenient, and rapid. The complete analysis, starting with the neutral solvents, can be carried out in about one hour.

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The Volumetric Determination of 8-Hydroxyquinoline

BY H. RONALD FLECK, F. J. GREENANE AND A. M. WARD, D.Sc., F.I.C.

DURING studies on the volumetric determinations of metals, by titrating hydrochloric acid solutions of the metallic complexes of 8-hydroxyquinoline, we have obtained indefinite and variable end-points in a number of cases. This variation is well illustrated by the results shown in the following table, in which Column 1 gives the volumes taken of a solution in *N* acetic acid of 8-hydroxyquinoline (A.R.) (20·500 grms. per litre, *i.e.* 1 ml. $\equiv$ 5·655 ml. of *N*/10-$KBrO_3$, assuming bromination to proceed according to the equation:—$C_9H_7ON + 2Br_2 \rightarrow C_9H_5ONBr_2 + 2HBr$). In all cases, 20 ml. of concentrated hydrochloric acid (approx. 12 *N*) were present, and the solution, contained in a stoppered bottle, was made up to 100 ml. with water. The volumes of *N*/10 potassium bromate solution (2·784 grms. of $KBrO_3$ and 12 grms. of KBr per litre), shown in Column 2, were then added, the solutions were allowed to stand for 5 minutes, 10 ml. of 10 per cent. potassium iodide solution were introduced, followed by starch solution, and the liberated iodine was titrated with *N*/10 sodium thiosulphate (Column 3). The results of independent duplicate determinations are shown.

Oxine solution ml.	$N/10$ $KBrO_3$ added ml.	$N/10$ $Na_2S_2O_3$ ml.	$N/10$ $KBrO_3$ used ml.	Calc. titre ml.
10·0	60·0	3·02, 3·15	56·98, 56·85	56·55
9·0	55·0	3·65, 3·89	51·35, 51·11	50·90
8·0	50·0	3·32, 4·04	46·68, 45·96	45·24
7·0	50·0	9·38, 7·88	40·62, 42·12	39·59
7·0	48·0	8·03, 6·26	39·97, 41·74	39·59
7·0	45·0	4·87, 4·33	40·13, 40·67	39·59
7·0	42·0	1·97, 2·12	40·03, 39·88	39·59
6·0	40·0	6·10, 4·63	33·90, 35·37	33·93

In these experiments, except in one case, when 6·0 ml. of oxine were used, the end-points were unsatisfactory. In those cases in which inexact end-points were obtained, a brown cloudiness developed during addition of the potassium iodide. If the solution cleared during the thiosulphate titration, the starch-iodide colour did not return after standing, but if a slate-blue solid was present at the end of the titration, the starch-iodide colour could be seen to return from this to the bulk of the liquid. Even when the titrations were carried out with vigorous shaking, the end-points were still unstable. It would appear that, in the unsatisfactory experiments, a part of the dibromo-oxine separated from solution, after addition of potassium iodide, possibly as a polyiodide, or the solid might be an adsorption complex of iodine and dibromo-oxine. Whatever the nature of the solid, the difficulty was completely avoided by adding carbon disulphide to the solution before adding potassium iodide, as follows:—

To the oxine solution in a stoppered bottle were added 20 ml. of concentrated hydrochloric acid, and the volume was made up to 100 ml. with water. Potassium bromate solution ($N/10$) was added in a fine stream, with swirling, until excess of bromine was present, as shown by removing a drop of the liquid and testing with starch-iodide paper (Bright and Fowler, *Bur. of Standards J. Research*, 1933, **10**, 333). After standing for 5 minutes the liquid was again tested to ensure that bromine was in excess, and 15 ml. of carbon disulphide were introduced. The mixture was shaken and bromine then passed mainly to the carbon disulphide layer. Ten ml. of 10 per cent. potassium iodide solution were added slowly, with shaking. A brown colour sometimes appeared at first, but rapidly changed to violet. Titration with $N/10$ sodium thiosulphate solution was then carried out, with shaking and addition of starch solution towards the end of the titration, until the colour of the aqueous layer changed sharply to a bright yellow-green tint. The end-points were permanent for at least an hour, the solid present at the end of the reactions had a pale brown silky appearance, and the carbon disulphide solution was not colourless, but pale brown.

Oxine soln. ml.	$N/10$ $KBrO_3$ ml.	$N/10$ $Na_2S_2O_3$ ml.	Titre ml.	Calc. titre ml.
10·0	59·10	2·28	56·82	56·55
8·0	48·00	2·62	45·38	45·24
7·0	41·00	1·43	39·57	39·59
4·0	23·50	0·90	22·60	22·62
2·0	12·10	0·74	11·36	11·31
1·0	6·15	0·47	5·68	5·65
0·5	3·00	0·19	2·81	2·82

The following experiments were made by the procedure with carbon disulphide described above, to establish (*a*) the time necessary for complete bromination, (*b*) the effect on the end-point of the excess of bromate used, and (*c*) the effect of varying the concentration of hydrochloric acid. The results given are the mean of two independent sets of observations, except when the values did not justify a mean being taken; both results are then given.

(*a*) Five ml. of oxine solution (≡ 28·28 ml. of $N/10$ $KBrO_3$); 20 ml. of concentrated hydrochloric acid; 75 ml. of water; 30·00 ml. of $N/10$ $KBrO_3$ were added in a fine stream; about 1 minute was required for the addition. The times of standing, after addition of the potassium bromate, are shown, and also the amount of $N/10$ potassium bromate consumed, based on the back titre with sodium thiosulphate.

Time: minutes	20	10	5	2	0
Titre: ml.	28·27	28·23	28·29	28·26	28·04

(*b*) Amounts of oxine, acid, and water as in (*a*).

Vol. of $KBrO_3$ added: ml.	28·70	28·70	28·70	28·70	35·00	35·00
Time of standing: minutes	10	5	2	0	10	5
Vol. of $KBrO_3$ consumed: ml.	28·22	28·23	28·18	28·15	28·33	28·35

(*c*) Oxine solution, 5 ml.; varying quantities of concentrated hydrochloric acid; water to total volume of 100 ml.; 30·00 ml. of $N/10$ $KBrO_3$ added, and titrated after 5 minutes' standing.

Conc. HCl: ml.	50	40	30	10	5	2	1
Vol. of $KBrO_3$ consumed: ml.	27·96	28·06	28·05	28·32	28·26	16·20	12·78
	28·37	28·52	28·27			14·04	11·73

In the experiments in which 10 ml. or less of hydrochloric acid were used crystals separated during the bromination. When 2 ml. or 1 ml. of hydrochloric acid were used it was not possible, after adding carbon disulphide and shaking, to see the colour of bromine in the carbon disulphide layer. On the addition of potassium iodide a pale colour, due to iodine, developed, and this increased during the titration with sodium thiosulphate until a maximum was attained; the colour then gradually decreased, until a very unstable end-point was reached.

The experiments described under (*a*), (*b*) and (*c*) were repeated with 5 minutes' standing, but without adding carbon disulphide. The results were substantially the same as when carbon disulphide was present, except that the end-points were sluggish and in (*b*) for experiments in which 35·00 ml. of $N/10$ potassium bromate solution were used, a blue solid was present after the starch-iodide colour was removed from the aqueous solution; the end-point was unstable, and the blue colour returned to the solution from the solid contained in the liquid.

Provided, therefore, that the concentration of oxine was such that, during the addition of potassium iodide, material did not separate and remain after the titration, the end-points were as satisfactory in the absence of carbon disulphide as in its presence; whatever conditions were chosen, however, provided the acid concentration was suitable, the procedure described, with carbon disulphide present, gave very sharp, exact and permanent end-points. Similar experiments

in the presence of carbon disulphide, made on a number of metallic complexes of the reagent, have given equally good results.

Attempts were made to replace carbon disulphide by chloroform or carbon tetrachloride, but in each case the slate-blue solid was formed and did not dissolve (or dissolved very slowly), and the end-points were therefore inexact. In the procedure with carbon disulphide the slate-blue solid does not appear, possibly because the adsorption complex (or polyiodide) is much more soluble in that solvent than in the others.

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Simplifications in the Method of Separation of Metals by Graded Potential

BY A. J. LINDSEY, M.Sc., A.I.C., AND H. J. S. SAND, D.Sc., PH.D., F.I.C.*

A CONSIDERABLE simplification of the electrolytic separation of metals by graded potential was introduced by Lassieur,† who replaced the potentiometer for the measurement of the potential difference between the auxiliary electrode and the cathode by a combination of a galvanometer and series-resistance of 26,000 ohms, which he used as an ordinary voltmeter.

Lassieur recognised that his voltage measurements were not correct, but, being repeatable, they were sufficiently accurate for his purposes. They are open to the obvious criticism that different workers using auxiliary electrodes of different resistances must employ different voltage readings. The following investigation was undertaken to determine the magnitude of the errors in Lassieur's voltages, and to make suggestions for such modifications of the method as would allow it to be more generally applied. The possible causes of error are:

1. Polarisation of the auxiliary electrode due to the current taken from it by the galvanometer.

2. The back-resistance of the auxiliary electrode. If the resistance of the auxiliary electrode is a, that of the galvanometer plus series-resistance g, the voltage read v, and the correct voltage e, then,

$$\frac{e}{v} = \frac{a+g}{g} \text{ or } e = v + \frac{va}{g} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The relative correction is thus a/g.

THE AUXILIARY ELECTRODE.—Lassieur employs a simplified $N/1$ calomel electrode consisting of $N/1$ potassium chloride solution in contact with mercury,

* NOTE. The experiments described in this paper were carried out by the former author, whereas the apparatus was designed by the latter.

† A. Lassieur, *Compt. rend.*, 1923, **177**, 1114; 1924, **178**, 847; 1924, **179**, 632; 1924, **179**, 847. *Bull. Soc. Chim.*, 1924, [iv], **39**, 1530. *Ann. Chim.*, 1925, [x], **3**, 235. *Bull. Soc. Chim.*, 1925, [iv], **39**, 1167. *Electro-analyse Rapide* (Paris, 1927).

the usual mercurous chloride being omitted. A certain amount of calomel will undoubtedly always form on the surface of the mercury in such an electrode, so that it will represent an approximation to a normal calomel electrode. In Lassieur's technique it is obviously desirable that the auxiliary electrode should have as low a resistance as possible. The electrode vessel previously described by one of us (ANALYST, 1929, **54**, 282) was modified with this end in view. It is shown in Fig. 1. The internal cross-section of the connecting arm has remained at about 4 mm., but the contracted bends, designed to prevent diffusion of the test liquid into the auxiliary electrode, have been replaced by bends of the shape shown that are not contracted. Of these, the double bend *a* (*vide* figure) is placed mainly outside the test solution, whereas the small single bend *b* is inside it. The

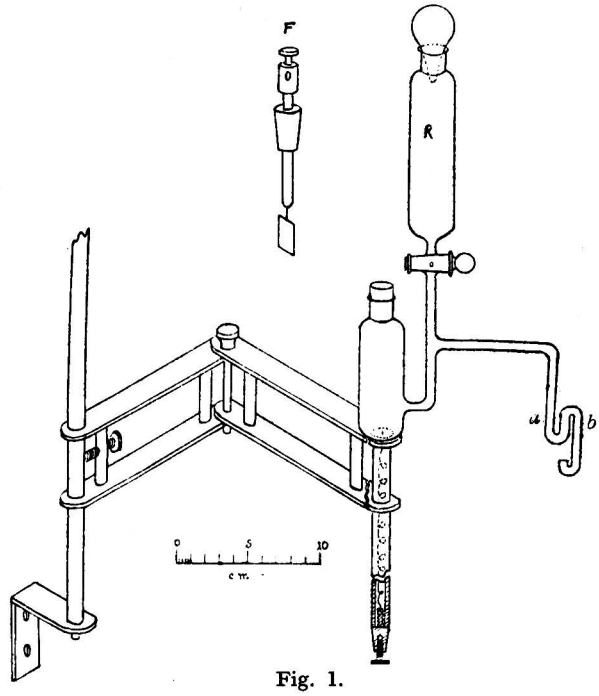


Fig. 1.

position of the reservoir funnel *R* has also been altered. It is now placed on the connecting arm, so that there is no chance of carrying liquid from the electrode-vessel into the test solution when the connecting liquid is being flushed out. The bracket for holding the electrode-vessel, which used to consist of a single adjustable arm, has now been replaced by the double-arm bracket shown in the figure. Much more ready adjustment is thus obtained. The electrode illustrated is fitted with a connecting wire for mercury, which may obviously be omitted when a platinum foil for use with quinhydrone is attached to the rubber stopper, as shown at *F*. Several different auxiliary electrodes, including Lassieur's potassium chloride electrode, fitted both without and with the filter-paper plug recommended by him, were made up and tested for polarisability and resistance. Their potential differences against a saturated calomel electrode were also determined.

The electrodes were:

TABLE I

MERCURY ELECTRODES

A	Hg | Hg_2Cl_2 | KCl. (N/1) |
B	Hg | Hg_2Cl_2 | KCl. (saturated) |
C	Hg | Hg_2Cl_2 | KCl. (solid) | $NaNO_3$. (50 grms./100 ml.) |
D	Hg | Hg_2Cl_2 | KCl. (solid) | $Na_2SO_4.10H_2O$. (20 grms./100 ml.) |
E	Hg | Hg_2SO_4 | H_2SO_4. (2 N) |
F	Lassieur's electrode (*op. cit.*, p. 58). Hg | KCl. (N/1) |

TABLE II

QUINHYDRONE ELECTRODES

G	Pt | acid KCl solution, saturated with quinhydrone
H	Pt | acid $NaNO_3$ solution, ,, ,, ,,
I	Pt | H_2SO_4 (N/1) ,, ,, ,,
J	Pt | HCl (N/1) ,, ,, ,,

All electrodes except F were set up in the vessel shown in Fig. 1. Solution G contained 25 grms. of potassium chloride and 1 ml. of N/1 hydrochloric acid per 100 ml. of solution, and solution H contained 50 grms. of sodium nitrate and 1 ml. of N/1 nitric acid per 100 ml. of solution.

TABLE III

Electrode		Polarisation (millivolts) after			
		½ hour	1 hour	1½ hours	2 hours
A	+	3	3	3	3
	−	2	3	2	2
B	+	1	1	1	1
	−	1	2	1	2
C	+	0	1	0	0
	−	0	1	0	2
D	+	0	0	0	0
	−	0	0	0	0
E	+	1	0	2	1
	−	0	1	2	2
F	+	25	82	109	122
	−	17	23	23	24
G	+	1	3	3	5
	−	5	7	8	8
H	+	6	9	8	9
	−	0	1	4	5
I	+	0	5	5	9
	−	0	0	2	2
J	+	0	0	0	0
	−	1	1	1	0

The polarisation of these electrodes was tested when a current of 20 micro-amperes (corresponding to a reading of one volt on our 50,000 ohms voltmeter)

was passing through them for varying periods in both directions. Their potentials against a saturated calomel electrode were measured by a potentiometer. In Table III the variations representing polarisations after the times stated are given in millivolts. The sign + indicates that the polarising current was leaving, the sign − that it was entering the electrode under test. The former case is the usual one in metal separations.

It will be seen that Lassieur's potassium chloride - mercury electrode is subject to great polarisation, and we do not recommend it for use as an auxiliary electrode during quantitative depositions. The polarisation of the mercurous salt - mercury electrodes is small and almost constant, and their use is recommended for the control of cathode potential.

The polarisation figures also show that the quinhydrone electrodes are suitable for auxiliary electrodes, but, as will be seen later, their resistances are variable and high, and on this account they are not suitable for Lassieur's high-resistance voltmeter technique. In connection with the polarisation of these quinhydrone electrodes it should be noted that, although the values after two hours are somewhat high, the original value may in every case be regained (within one or two millivolts) by rocking the platinum electrode in the solution.* The figures quoted are those obtained by measurement of the potential after the electrode and solution had remained perfectly quiescent for the period stated.

ELIMINATION OF THE ERROR DUE TO THE BACK RESISTANCE OF THE AUXILIARY ELECTRODE.—The galvanometer we have used as a voltmeter is a pointer instrument of the unipivot type of a little under 1000 ohms internal resistance, marketed as type L by the Cambridge Scientific Instrument Company. We have had it fitted with a series-resistance so as to give a full-scale reading on a mirror-backed scale at 1·2 volts. It is calibrated in centivolts so that millivolts may be estimated with fair accuracy. The total resistance is 50,000 ohms, and the series-resistance may be short-circuited by means of a shunt actuated by a button. It will be seen that the instrument will detect a current of about 0·02 micro-ampere (corresponding to 1 millivolt), and can therefore be used as a detecting galvanometer for many purposes. It was thought not only that an instrument of this type could be used as a voltmeter for routine work in Lassieur's technique, but also that it might be possible to design a simple potentiometer assembly of the voltmeter-potentiometer type (Tafel, *Z. physikal. Chem.*, 1905, **50**, 662; Sand, *J. Chem. Soc.*, 1907, **91**, 380), constructed mainly of wireless fittings to which our voltmeter could be attached and, at the will of the operator, either play the part of an independent direct-reading instrument, or be used as part of the potentiometer first in the capacity of a zero instrument, and then in that of a voltmeter. Fig. 2 (omitting the dotted portion) shows the wiring diagram adopted, and Fig. 3 gives a view of the completed box, including the dry cell, as constructed for us by Messrs. Griffin & Tatlock.

The assembly has four terminals, two of which (marked "voltmeter," Fig. 2) are connected with our instrument, the other two (marked *X*) being joined to the

* NOTE. It has been pointed out to one of us by Professor C. Drucker, of Leipzig, that the temporary polarisation referred to may be avoided by using horizontal platinum electrodes on which solid quinhydrone is placed.

points to be controlled. The battery is first put in circuit by pulling out the push-pull switch. The latter is arranged so that to close the box the switch must be off. If it is desired to know the reading of the voltmeter when connected directly with the points X, the double pole throw-over switch A is first put in the position "To direct." It is then altered to the "To potentiometer" position. The voltmeter now acts as a zero instrument between the coarse-adjustment slider S_c and the point X_+. In order that it should give a positive reading, the zero point of S_c should be at the extreme + end of the potentiometer. S_c is then moved until the voltmeter registers zero. The fine adjustment is then completed by means of the fine adjustment slider S_f, the button for cutting out the back resistance of the voltmeter being depressed. This button is then released and the morse-key M depressed. The voltmeter then registers the P.D. between the points

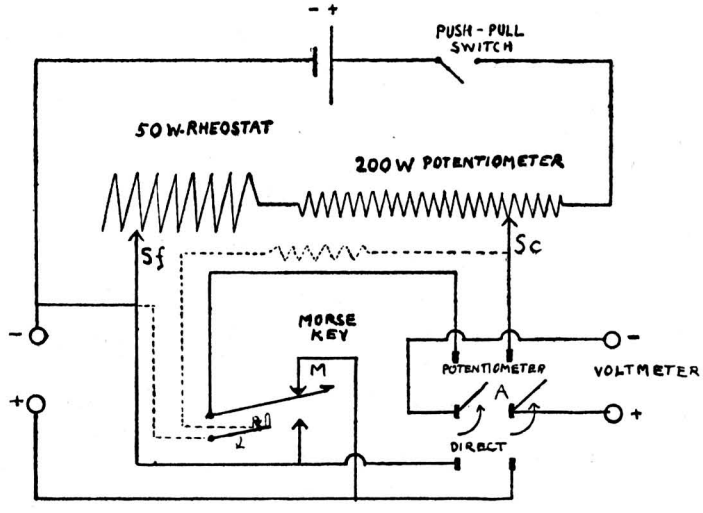


Fig. 2.

S_f and S_c that has previously been balanced against the potential difference between X_- and X_+. It will be remembered that in the original potentiometer the voltmeter remained in parallel with the variable points S_c and S_f, while the potential difference between X_- and X_+ was being balanced against that between S_c and S_f, with the aid of a separate zero instrument. With the present arrangement the voltmeter cannot remain shunted across S_c and S_f while it is being used as a detector instrument, and it therefore becomes necessary to examine what is the maximum error that may be introduced hereby.

If E be the total E.M.F. of the potentiometer circuit, X the P.D. between S_c and S_f, R the total resistance, and r the resistance between S_c and S_f, then obviously $X = Er/R$.

When the voltmeter is placed in parallel with r, X is altered, since both r and R undergo a slight diminution, which is manifestly the smaller the higher the resistance of the voltmeter. As the calculation of the error is somewhat lengthy, we give only the result. It is found with sufficient accuracy, that the

maximum error occurs when $r/R = 2/3$, and is then equal to $(4/27)ER/g = 0{\cdot}15ER/g$, g being the resistance of the voltmeter.

For the dry cell we may take $E = 1{\cdot}5$ volts, for our potentiometer $R = 250$ ohms, and for our voltmeter $g = 50{,}000$ ohms. We thus find that the maximum error occurs at readings of about one volt, and then amounts to 1·1 millivolts. If an error of this magnitude is not permissible it can be reduced by reducing the resistance R of the potentiometer circuit, or it may be eliminated altogether by placing a resistance equal to that of the voltmeter in parallel with r during

Fig. 3.

balancing, and having this automatically switched out when the voltmeter is in use as such. An arrangement of this kind is shown in the dotted portion of the diagram. The potentiometer gives an accuracy which is limited by that of the voltmeter, and for readings of about one volt should, therefore, be the same as that of the Cambridge portable ionisation potentiometer. The absolute accuracy of the readings is uniform throughout, whereas that of the Cambridge potentiometer increases for smaller readings. We have frequently used our potentiometer for p_H measurements and other physico-chemical laboratory exercises.

For purposes of gravimetric electrolytic analysis the potentiometer need only be applied once, after the auxiliary electrode has been selected. The direct-reading voltage v against any arbitrarily chosen working electrode, say copper in copper sulphate solution, and the correct voltage e, are determined. Hence the

relative correction $a/g = (e - v)/v$ may be calculated; and by means of it, using equation (1), the correct voltage e from any subsequently measured direct-reading voltage v. Knowing $g = 50{,}000$ ohms, the resistance a of the auxiliary electrode may be determined.

In Table IV, column 2, the resistances of some of the auxiliary electrodes tabulated in Tables I and II are given. Column 3 contains the resistances when the ends have been plugged with small tightly-rolled filter-paper plugs, as recommended by Lassieur, and in column 4 is the P.D. of each electrode referred to the saturated calomel electrode.

TABLE IV

Electrode	Resistance in ohms		Potential referred to saturated calomel electrode
	Unplugged	Plugged	Millivolts
A	2200	2600	+ 34
B	820	870	0
C	500	550	− 9
D	3000	3300	0
E	250	260	+426
F	2000–2500	2500–3000	+ 15 to +40
G	1000–7500	variable	+353
H	2000–11,000		+350
I	650–2600		+440
J	250–2000		+450

The above figures show that the mercury - mercurous salt electrodes are suitable as auxiliaries when Lassieur's technique is used, since the resistance is constant. Electrodes B, C and E may be used connected directly with the 50,000-ohm voltmeter without correction, since the error is about 1 per cent. or less, and it is never necessary to control the cathode potential during a separation to within less than one centivolt. These three electrodes (with the addition of D, for which readings need to be corrected) are all that are necessary in analysis, since they contain respectively chloride, nitrate and sulphate junction liquids, and one of these should be suitable for any analysis.

The resistance of the quinhydrone electrodes varies with time. A clean platinum plate gives a low resistance which usually increases rapidly. Constancy is not attained within 8 to 10 days, and great variations in resistance may occur within a limited period. Evidence has been obtained in favour of a supposition that a highly non-conducting film is formed over the surface of the platinum in this type of electrode. These half cells are useless for Lassieur's method, although, since their potential is almost constant, they may be used in conjunction with a potentiometer. It is interesting to note that when tested with alternating current, such electrodes show approximately the normal resistance to be expected for the electrolyte taken. The question was specially examined whether there is any risk of electrolyte from the beaker being lost by finding its way past the bends into the auxiliary electrode. Liquids lighter and also heavier than the solution in the auxiliary electrode were examined. The 50 per cent. sodium nitrate electrode (Table I) was used, and the bent contact arm was dipped into coloured solutions, which were stirred for 15 minutes by means of the usual electrolysis apparatus.

Potassium permanganate solution (about $N/20$) was treated in this way, and at the end of the time but very little colour had diffused into the first bend. This colour was readily flushed out by a few drops of liquid from the funnel. A similar result was obtained with the potassium permanganate at the boiling-point. With saturated sodium nitrate solution in the beaker, *i.e.* a liquid heavier than that in the electrode vessel, diffusion occurred to a greater extent after 15 minutes' stirring. The colour, which had ascended to about half the height of the vertical limb, was readily flushed out by means of a few ml. of the electrolyte from the tap funnel. (It should be noted that most solutions for analysis are less dense than saturated sodium nitrate solution, and, therefore, are less liable to enter the electrode.)

Solutions of scarlet eosine, when treated in the same way, gave similar results, but were precipitated in the contact limb. The coloured precipitate was easily removed by flushing.

We may summarise our investigation by stating that Lassieur's suggestion to control the P.D. between the auxiliary and working electrodes, by what we may term an ultra-high resistance voltmeter, effects a considerable simplification. We do not favour the mercury electrode, suggested by Lassieur, in which the calomel is omitted. We have described further modifications of the auxiliary electrode vessel and a potentiometer arrangement, made from simple fittings, by means of which the correction to be applied to direct readings may be readily determined for any given auxiliary electrode. We recommend that published figures should always contain corrected voltages. The potentiometer we have described may also be employed for p_H and other measurements.

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

Experiments on the Electrolytic Analysis of Certain Alloys of Antimony, Copper and Tin

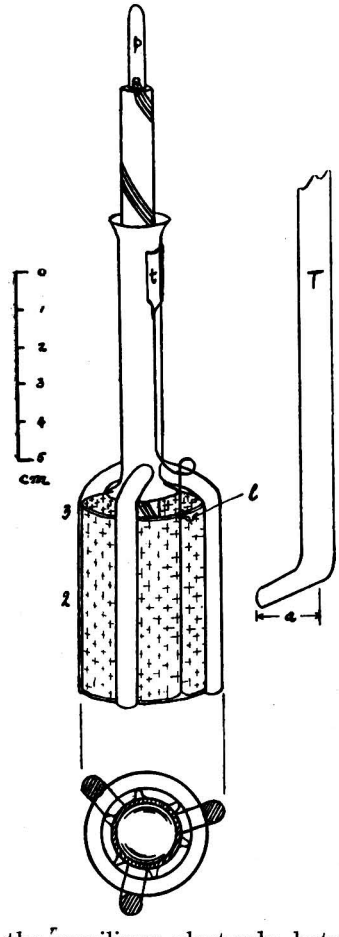
BY A. J. LINDSEY, M.Sc., A.I.C., AND H. J. S. SAND, D.Sc., PH.D., F.I.C.*

THE gravimetric analysis of alloys of copper, antimony and tin is generally considered one of the most troublesome determinations in analytical chemistry, and the test of the electrolytic method with the apparatus described in the preceding paper was, therefore, deemed to be of some interest.

The working electrodes used were developed from those previously described by one of us (ANALYST, 1929, **54**, 277). The assembly of the two electrodes and the tripod frame is shown in the figure. The inner electrode is now generally made of pyrex glass instead of quartz glass, the former being the more easily obtainable. The four connecting wires, usually of 0·4 mm. in diameter, are led up outside the electrode in the same manner as when it is made of quartz, but the construction is somewhat simplified, as it is now possible to "catch" (*i.e.* lightly fuse) the wires,

* NOTE. The experiments described in this paper were carried out by the former author, whereas the apparatus was designed by the latter.

as well as the gauze, on to the surface of the glass. The stem has an outside diameter of about 8 mm. The construction is usually further simplified by leaving the tube forming the stem completely open, and providing a seating for the lead, which is used as a cement for the silver leading-in peg, *p*, by means of a plug of asbestos wool. The collar formed by the lead must have a wall-thickness of at least 1½ mm., so that there may be sufficient room for its plasticity to come into play, and that cracking may be avoided during changes of temperature. The top of the stem must be rounded-off by fusion. The lead is preferably freed from oxide by melting it, not in its ultimate position, but either in an extension of the stem, which may be cut away later, or in a little funnel made from a tube drawn to a capillary. In either case the oxide is left behind when the lead is run into position.



The quartz-platinum outer electrode has been abandoned and replaced by a platinum cylinder, which is held in position by the separate glass tripod shown. With this arrangement the weight of the platinum need be no greater than in the quartz-platinum electrode. The electrodes we have used weighed between 9 and 10 grms. The method of holding the electrodes has remained essentially the same. The stem of the inner electrode is slipped through the guide tube of the tripod and fitted into its holder or chuck; the outer electrode is pushed inside the tripod, and both it and the tripod are held by the cathode clamp. The leading-in wire, about 0·8 mm. in diameter, is welded to the bottom of the gauze electrode cylinder and attached loosely by a wire loop, *l*, to the top. This construction ensures enough "give" to prevent the wire from breaking on being bent or as a result of vibration. The leading-in wire ends in a tab, *t*, which is held between the tripod and the metal face of the clamp when the electrode is in use. The outer electrode can be taken from the stand without removing the inner one. A cylinder has an advantage over a bell-shaped electrode, since a metal deposit may be removed from it, for further analytical treatment, with a smaller amount of acid. We have found it quite suitable for separations by graded potential, such as that of bismuth or antimony from lead. The tripod is placed in such a position that there may be room for the bend of the auxiliary electrode between two of the legs, the tip of the contact arm being about one cm. below the top of the electrode. The diameter of the outer electrode is 3·2 cm. and its height 5 cm., the diameter of the gauze coating of the inner electrode being about 2·5 cm., and its height about 2·5 cm. In these circumstances the lines of flow of the current should be confined practically to

the space between the two electrodes, and the potential difference between the outer electrode and various points in the electrolyte behind and above it should have the same value.

Table I gives the electrode potentials observed when the tip of the auxiliary electrode was at the positions 1 and 3 (see figure), those obtained when it was at 2 being made equal to zero. The solution electrolysed for these experiments was an acid solution of copper sulphate containing 0·25 grm. of copper per 100 ml.

TABLE I

Current in amperes	Electrode potential in millivolts at positions: 1	2	3
0·5	5	0	10
1·0	12	0	7
1·5	15	0	10
2·0	15	0	5
2·5	10	0	20
3·0	10	0	10

It is obviously necessary that the three legs of the glass tripod should have a distance from the axis of the guide tube which is accurately equal to the radius of the electrode cylinder. This can be attained easily in the manufacture of the tripod, when bending the legs into position, by making use of the template, *T*, consisting of a tube or rod which can be pushed into the guide tube, which it fits accurately, the length *a* being equal to the radius of the electrode cylinder.

The method of analysis we have tested is similar to that of Lassieur (*Electro-analyse Rapide*, p. 191), but certain modifications have been found necessary.

The sample (about 0·3 grm.) is dissolved by warming with 10 ml. of concentrated hydrochloric acid, solution being aided, if necessary, by the addition of small quantities of potassium chlorate, and the chlorine being finally boiled off. It is desirable to add 10 ml. of 10 per cent. ammonium chloride solution before the use of chlorate, since, otherwise, tin appears to volatilise as tetrachloride during boiling. When the solution is prepared, 5 ml. of concentrated hydrochloric acid and 1 grm. of hydroxylamine hydrochloride are added, and the solution is diluted to about 100 ml. Electrolysis is commenced with an auxiliary electrode potential of not above 0·40 volt (saturated calomel) at a temperature of 65 to 75° C. At this constant potential the current fluctuations mentioned by Lassieur (*op. cit.*, p. 192) are observed, and a residual current of about 0·3 amp. is attained in about 25 minutes. The auxiliary electrode is flushed out, and the beaker washed down at this stage, after which, electrolysis is allowed to continue for another 5 to 10 minutes. The mixed deposit of copper and antimony is weighed and dissolved in a mixture of 5 ml. of nitric acid (1·42) and 5 ml. of hydrofluoric acid (40 per cent.), and the solution is diluted to 100 ml. The deposition of copper is then carried out precisely as described by Lassieur. Tin may be determined in the liquid from which the copper and antimony have been separated by adding 1 grm. of hydroxylamine hydrochloride and electrolysing at 1 to 1·5 amp. for 15 to 20 minutes. Potential control aids the formation of a good deposit, the saturated calomel

electrode being kept at 0·60 volt for most of the time, and, finally, being raised to 0·80 volt.

The following are experimental results obtained by the above method on mixtures of the three pure metals, which were weighed out separately and dissolved together as though they were present in an alloy:

	Taken Grm.	Found Grm.	Taken Grm.	Found Grm.	Taken Grm.	Found Grm.
Copper	0·0135	0·0138	0·0118	0·0128	0·0114	0·0116
Antimony	0·0421	0·0424	0·0488	0·0487	0·0698	0·0698
Tin	0·3045	0·3027	0·3078	0·3063	0·3	—
Copper	0·0122	0·0129	0·0122	0·0126		
Antimony	0·0413	0·0409	0·0413	0·0409		
Tin	0·3	—	0·3	—		

As will be seen, the method is good for the determination of copper and antimony, but is only moderately accurate for tin. Errors of 2 to 3 mgrms. have been obtained with 0·3 grm. of tin. This agrees with the work of Furman (*J. Ind. Eng. Chem.*, 1923, **15**, 1071), who, in criticism of Lassieur's method, states that he always found 1 to 3 mgrms. of tin missing in his analyses (see also Lassieur's defence, *Compt. rend.*, 1924, **179**, 827).

It appears that, in view of the heterogeneous nature of such alloys as these (Lassieur, *op. cit.*, p. 192), the method is sufficiently accurate for most purposes, and has the advantage of rapidity over other gravimetric methods.

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

Errata.

The Excretion of Aloes (March issue), p. 154, line 3.—*For* "200 mgrms." *read* "300 mgrms."

The Analysis of Fruit and Fruit Products (April issue).—In the tables on pp. 244–247 the expression

"Mean 1·25SD Mean 2SD"

should read

"Mean *minus* 1·25SD Mean *minus* 2SD"

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 USE OF COMPLEX IONS AS INDICATORS IN ANALYSIS

Indicators for Metals, Etc.

If we consider the equilibrium between a complex ion, such as $Ni(CN)''_4$, and its components in solution, we must have at all concentrations the mass action relation $[Ni(CN)_4'']/[Ni^{\cdot\cdot}] = K[CN']^4$, where K is a constant. This equation is analogous to that for the dissociation of an indicator in alkalimetry, and the complex ion may be used in titrations involving the disappearance of cyanogen ion, instead of hydrogen ion, provided we have a suitable means of estimating either $Ni(CN)_4''$ or $Ni^{\cdot\cdot}$ in solution. Organic reagents for the detection and determination of metallic ions have been largely applied within recent years; where a suitable reagent is available, and certain other conditions are fulfilled, a means can be developed of titrating certain metals in solution.

The method is best illustrated by an example. In principle, any complex (*e.g.* a fluoride or an oxalate) might be used, but only the complex cyanides will be described here. For the purposes of analysis, it is essential that the equilibrium between the complex and its components be set up fairly rapidly, as is the case with such metals as mercury, gold, silver, copper, zinc, cadmium, and nickel. The complexes formed by tervalent iron and cobalt, on the other hand, require too much time for their formation to make them suitable.

A typical reagent, containing the nickel cyanide complex, is made up as follows:—Five per cent. potassium cyanide solution is diluted with an equal volume of alcohol, and excess of solid nickel dimethylglyoxime is added to the solution, which is then boiled and allowed to stand for some time before filtering. The filtrate consists of a saturated solution of nickel cyanide in potassium cyanide, together with free dimethylglyoxime. It is best used at one-tenth the above strength, and will not have the maximum sensitivity unless it has been completely saturated with nickel dimethylglyoxime. If kept over long periods of time, it may require occasional re-filtering.

This reagent may be used in one of two ways:

(A) As a qualitative reagent for those metals, the cyanides of which are less dissociated than that of nickel. In this way the metals, silver, mercury (mercurous and mercuric), cadmium and gold, were found to be detectable when 1 ml. of a 10^{-4} *M* solution was added to 3 ml. of the nickel reagent. Owing to the presence of free dimethylglyoxime in the reagent, nickel also gives a positive reaction, but is distinguished from the above ions by also giving a pink colour with dimethylglyoxime solution. Excess of free acid interferes with the test, but may be neutralised by adding sodium bicarbonate.

The test depends upon the appearance of a pink turbidity, which has a characteristic silky look when viewed against strong diverging light. Ions such as magnesium, beryllium, antimony, bismuth, tin or thallium, which do not form cyanide complexes, give no reaction, but some of the tervalent metals, such as iron and aluminium, form a small amount of gelatinous precipitate at concentrations of about *M*/100, and this is coloured somewhat pink by adsorption of the nickel complex. Bivalent iron attacks the complex only in boiling solution, and zinc, copper and lead interfere with the reagent. The time required for completion of the test increases with dilution, but never exceeds ten minutes.

Test for Formaldehyde.—The reagent was found to be particularly sensitive as a test for formaldehyde. With 3 ml. of a 5.10^{-7} *M* solution added to 1 ml. of reagent a definite silkiness was observed at the end of about one hour, as compared with 3 ml. of distilled water added to 1 ml. of reagent. With acetaldehyde the limit of the test is about 10^{-5} *M* in the same time, and the tests are so faint in comparison with formaldehyde that the reagent can be used to detect it in the presence of acetaldehyde. Schiff's reagent, used under comparable conditions, gave a limit test with formaldehyde in about the same time, at a concentration of 5.10^{-6} *M*.

(B) A few drops of the indicator may be added to standard potassium cyanide solution in a flask, and solutions of salts of silver, mercury or copper run in until a pink colour appears. In principle, all the potassium cyanide is used up before the complex is attacked, but with mercury salts the rate of attack is so slow that it is better to add them to excess of cyanide, and to allow the mixture to stand for some time before back-titrating with silver nitrate. With cadmium salts, the end-point appears to coincide with the formation of the complex $KCd(CN)_3$, but the end-point is not considered as completely satisfactory. Gold salts were not tried, but with *N*/10 silver nitrate solution excellent end-points were obtained, even in artificial light, since the pink nickel compound appears in a fine colloidal form. The last few drops should be added with shaking, and at intervals of not less than thirty seconds. When the titration is complete, a fresh portion of standard cyanide solution may be added to the flask. This re-dissolves the indicator, which may be used in further titrations. The end-point is assumed to coincide with the formation of $KAg(CN)_2$, and is very consistent. In this connection it should be noted that *N*/10 solution of potassium cyanide was observed to lose in strength at the rate of about 0·3 per cent. per day.

USE OF OTHER CYANIDE COMPLEXES.—Attempts were made to use the complex cyanides of cadmium and mercury, in conjunction with diphenylcarbazide, to indicate the liberation of the free ions. Reagents made by dissolving isatin and cuprous cyanide in potassium cyanide solution, and cupric diethyldithiocarbamate in potassium cyanide solution were likewise tried. None of these was as satisfactory as the nickel reagent, partly owing to the fact that the organic indicator used was not sufficiently specific. The extension of the method depends, to some extent, on the discovery of more specific reagents for the metals whose complexes are used, and also on the use of other negative ions besides cyanogen.

DEPARTMENT OF THERMODYNAMICS
CLARENDON LABORATORY, OXFORD
A. R. UBBELOHDE

VARIATION IN THE PHOSPHORUS-CONTENT OF MAIZE MEAL USED IN RACHITOGENIC RATIONS

THE Steenbock rachitogenic diet 2965 (Steenbock and Black, *J. Biol. Chem.*, 1925, **64**, 274) consists of the following parts:—Yellow maize (meal) 76, wheat gluten 20, calcium carbonate 3, sodium chloride 1. It should give a Ca/P ratio of 4 to 1, and it is essential for the development of corresponding rachitic conditions in rats and for the production of a similar degree of rickets at will that the ratio should not vary much from this value. The object of this note is to draw attention to the possibility of the ratio being variable, owing to considerable fluctuation in the phosphorus-content of yellow maize drawn from commercial sources, and that the ration should not be fed before a chemical analysis of the constituents has been carried out and the calcium carbonate adjusted to suit the Ca/P ratio.

The calcium in 100 grms. of the ration, allowing for an average of 97 per cent. purity of the $CaCO_3$ (on a calcium basis), for 0·016 per cent. of calcium in the maize and 0·140 per cent. in the wheat gluten, is 1·246 grm. The phosphorus-

content should then be 0·312 grm. Wheat gluten contains an average of 0·234 (0·193 to 0·275) per cent. of phosphorus, and would account for 0·047 grm., leaving the maize (76 parts) to supply 0·265 grm. The maximum permissible phosphorus-content of the maize is, therefore, 0·265/0·76=0·349 per cent. of air-dry material.

Holmes and Tripp (*Cereal Chem.*, 1933, **10**, 313) have observed a considerable variation in the phosphorus-content of yellow maize grown in the United States, whilst Neal and Becker (*J. Agric. Res.*, 1933, **47**, 249) have found a variation of 0·291 to 0·332 per cent. according to soil conditions. Armsby (*Nutrition of Farm Animals*, New York, Macmillan, 1922, p. 723) gives the average phosphorus-content of maize as 0·303 per cent. (21·5 per cent. of the ash).

During the past few years a considerable number of maize samples from local merchants have been analysed. Widely varying values, mostly higher than the above, have been obtained. The following table illustrates these variations, and gives the Ca/P ratios which would have resulted if such maize had been included in the Steenbock diet.

Sample	Calculated on air-dry maize			$\frac{100P}{Ash}$	Ca/P ratio
	Moisture Per Cent.	Ash Per Cent.	Phosphorus Per Cent.		
1	11·16	2·32	0·524	22·6	2·80
2	12·67	1·58	0·382	24·2	3·70
3	12·99	1·52	0·380	25·0	3·71
4	12·48	1·47	0·360	24·5	3·88
5	8·49	1·51	0·355	23·4	3·93
6	12·84	1·52	0·354	23·3	3·94
7	9·99	1·55	0·345	22·3	4·03
8	11·85	1·23	0·278	22·5	4·82
(Armsby	—	1·41	0·303	21·5	4·49)
				Average 23·2	

Six samples of flaked maize gave the following results, respectively:— Moisture, 11·15, 16·60, 15·28, 11·32, 13·95, 13·34; ash, 1·61, 1·60, 1·48, 1·41, 1·42, 1·34; phosphorus, 0·345, 0·341, 0·314, 0·297, 0·297, 0·286 per cent. There was an average of 21·2 (20·9 to 21·4) per cent. of phosphorus in the ash.

Other maize by-products showed a greater variation in ash-content and the phosphorus-content of the ash. The source and type of the maize were, of course, unknown. Seven samples of maize germ meal varied in ash-content from 2·22 to 6·51 per cent., and the phosphorus from 12 to 23 per cent. of the ash. Hominy chop, which contains the bran of the seed, has a higher ash-content than the seed (2·1 per cent.) and phosphorus varying from 19·1 to 23·7 per cent. of the ash. The ash (and the phosphorus) appears to be concentrated in the germ and the bran of the maize seed, and it is obvious that seed containing the greatest proportion of starch to bran plus embryo will have the lowest phosphorus-content. The regularity of the proportion of phosphorus to ash in the seed (average 23·2 per cent.) may be used as an index of the approximate phosphorus-content. It is suggested that the diet may be made up on this approximate basis; the adjustment of the calcium could then be made on the results of analysis of the whole diet.

The table illustrates a range of Ca/P ratio from 2·8 to 4·8 if the recipe for the diet is taken without analysis of the constituents. The importance of analysis, therefore, is obvious, and is further enhanced by possible fluctuations in the moisture-content of maize (most samples, however, contain roughly 12 per cent.) and the possibility of variation in the calcium- and phosphorus-contents of various batches of wheat gluten.

W. L. DAVIES

NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING
SHINFIELD, READING

A NEW METHOD OF APPLYING THE PRECIPITIN TEST

THE method here described is one which, in the opinion of the author, offers certain advantages over the test-tube and capillary-tube methods. It was devised originally for dealing with small quantities of fluids such as the alimentary canal content of mosquitoes and other blood-sucking insects, and it serves this purpose very satisfactorily.

Drops of antiserum are placed on microscope slides and, by means of a glass style, are spread over a small area to form circular films. The films are allowed to dry, and drops of the various test fluids are then deposited on the films. The slides are placed in a moist chamber and examined, after an interval of thirty minutes, under the low power of a microscope.

In a positive reaction the film of antiserum becomes markedly granular, and when disturbed breaks up into insoluble granular fragments, which may in many cases be easily observed with the naked eye. When the reaction is negative the film of antiserum goes into clear solution, and no granular particles are observable microscopically.

A similar method may be used for the approximate estimation of the protein concentration of the fluids under examination. A drop of the fluid is placed on a dry film prepared with a 1 per cent. solution of tannic acid and 1 per cent. acetic acid in physiological saline, and the result is compared with those obtained with serum dilutions of known strength.

The use of drop preparations has proved very serviceable in the testing of insoluble proteins. For example, it was found possible to establish the human origin of a blood stain which had been immersed for three weeks in absolute alcohol; and experimental evidence indicates that in certain protein conjugates, such as protein tannate and picrate, the protein retains its power of being specifically agglutinated when presented as a fine suspension.

Further work on the specific agglutinability of insoluble protein compounds is being carried out, and the results obtained will be reported later.

I have to thank the Director of Medical Services, Uganda, for permission to publish this note.

L. C. HADDON

LABORATORY SERVICES
KAMPALA, UGANDA PROTECTORATE

THE PERKIN TUBE

MR. GARDINER'S note on the Sprengel tube (ANALYST, 1934, 172) reminds me that, while references to the Sprengel tube are fairly frequent, one hardly ever sees mentioned the modification of it devised by Sir W. H. Perkin, and it looks as though this has been forgotten.

Yet the Perkin tube presents great advantages over the Sprengel tube in ease of manipulation; it permits of very accurate work, and it can be readily made, of any size down to very small capacity, by anyone with the very slightest acquaintance with glass-working. The one thing to be careful about is to see that the capacity mark on the one limb is as nearly as possible in the line of the other limb produced backwards. I feel that I am doing chemists a service in drawing their attention to it.

It is figured and described in the *J. Chem Soc.*, 1884, **45**, 443, and an improved form (which is also figured in Thorpe's Dictionary, under "Specific gravity") in the same journal (1896, **69**, 1043).

The apparatus is simply a U-tube, with either end drawn out into a capillary, and these capillaries bent outwards so as to be at right angles to one another. One limb of the U-tube is kept a little shorter than the other, and, in drawing off

the capillary at this side, a slight enlargement or bulb is left near its end. The other capillary ends in a narrow point. When the tube is inclined so that this capillary is horizontal, a mark is made on the other capillary (then vertical), at the same level as the horizontal capillary.

The tube is filled by suction, above the mark, and hung in a beaker of water at the desired temperature, until equilibrium of temperature is established. It is then tilted until the exit capillary is horizontal (the shortened limb allows the whole, except the capillaries, to remain under water), and liquid is removed by filter paper until the liquid in the vertical capillary reaches the mark, when the tube is restored to the normal position, and is ready for weighing.

When the tube is righted, the liquid retreats from the point, and no evaporation from the point is to be feared; it rises in the other capillary, and the little bulb provides for any expansion of the liquid, if the temperature of weighing is higher than that at which the density is to be determined.

J. T. DUNN

10, DEAN STREET
NEWCASTLE UPON TYNE

ERASURES AND OFFSETS IN INK WRITING

IN the case of *Watts* v. *L.C.C.*, heard in the King's Bench Division, in November, 1932, a legal document was produced bearing an ink mark which might have been made by erasure of a pen stroke or by other means. To determine this point, a microscopic examination with reflected illumination was made, and in conjunction with this, numerous experimental erasures were prepared with a variety of papers,

Fig. 1. (Erasure) ×18.

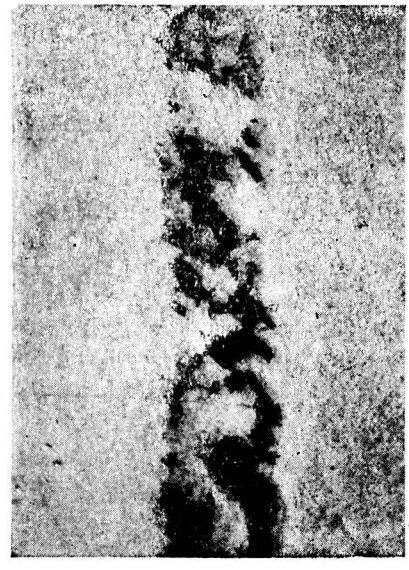


Fig. 2. (Offset) ×18.

inks and methods of erasure. In each of these experiments the surface of the paper was more or less roughened, and some of the fibres were distorted, partly broken or fibrillated. None of these characteristics was present in the mark under examination, and the distribution of the ink pigment was different in the two cases.

These negative results suggested that the mark in question might be an offset from a wet ink stroke on the same or another document, and a number of marks produced in this manner showed considerable resemblance to the one under examination. The accompanying illustrations depict, under a low magnification (× 18), examples of these markings, Fig. 1 showing a partial erasure, and Fig. 2 an offset.

The characteristics of an offset are as follows:—No roughening of the paper surface is apparent, and no loose, broken or frayed fibres are present. The patches of ink pigment forming the mark are usually well defined, with clear-cut edges, often bounded by the paper fibres, and the fibres above the general surface of the paper are evenly pigmented or show a gradual change in intensity along the fibre.

The lightly pigmented surface fibres are usually bordered by fine dark lines where the ink has collected in the rounded angle on either side.

Partial erasures, on the other hand, whether made with rubber, ink-eraser or a knife blade, show more or less diffused edges to the patches of pigment remaining, and very irregular pigmentation on the fibres above the paper surface, whilst lightly tinted fibres with dark borders are rarely met with, even on rough-surfaced papers.

T. J. WARD

THE LABORATORY
STAG BREWERY, PIMLICO, S.W.1

Official Appointments

THE Minister of Health has approved the following appointments:

FREDERICK GRANT DUNCAN CHALMERS as Public Analyst for the County Borough of Wolverhampton, in place of A. E. Johnson (deceased) (March 23rd, 1934).

THOMAS REGINALD HODGSON as Public Analyst for the Borough of Hyde, in place of A. E. Johnson (deceased) (March 22nd, 1934).

HENRY TURNER LEA as Public Analyst for the County Borough of Burton-on-Trent, in place of William Partridge (deceased) (March 29th, 1934).

ROY WARREN WATRIDGE as a Public Analyst for the County Council of the Isle of Wight, in addition to S. Ernsley (April 16th, 1934).

HUGH AMPHLETT WILLIAMS as a Public Analyst for the Metropolitan Borough of Deptford, in addition to H. G. Harrison (April 12th, 1934).

Notes from the Reports of Public Analysts

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

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1933

THE number of samples of foods and drugs examined under the Food and Drugs Act during the quarter was 978, and the total number during the year was 3655, of which 87 were adulterated. In addition, 3377 samples of milk from individual cows and herds were examined.

MOULD IN BUTTER.—One of the 91 samples submitted during the quarter contained a large number of black spots. These were found to be due to the growth of a mould, the mycelium of the mould running right through the butter.

FISH SOLD UNDER WRONG NAMES.—Four of the 15 fish submitted were found to be untrue to name. The fish purported to be hake, whereas either ling or coalfish had been sold instead.

COMPOSITION OF SHODDIES.—Of the 193 samples of shoddy examined under the Fertilisers and Feeding Stuffs Act, 123 were sold at "unit value," and 12 without a guarantee. Of the 58 samples sold with a warranty, 18 contained too little nitrogen, the deficiencies ranging from 1·3 to 2·32 per cent. With the exception of one sample, which contained 28·8 per cent. of water, the nitrogen deficiencies were not due to excessive water. Many of the shoddies contained considerable quantities of mineral matter, and in almost every instance these shoddies were either fleece combings or wool dust. Five of the samples of fleece combings contained 30 per cent. or more of mineral matter, and the worst sample contained 36·4 per cent. In addition, several of these samples were damp—a condition that has not existed for several years. The results indicate the importance of obtaining a warranty on the purchase of shoddy, or of buying only at "unit value."

Wool Shoddy Manure.—I took exception during the quarter to the sale of some material which was sold as "Wool Shoddy Manure," and which contained only 3·4 per cent. of nitrogen. This manure consisted almost entirely of cotton and vegetable fibre, and I considered, therefore, that it was misdescribed. In my opinion, a wool shoddy should contain at least 50 per cent. of wool, otherwise the term is misleading. The manure could very properly have been sold as a flock dust, and this would not have implied any material proportion of wool. The implied definition contained in the Fertilisers and Feeding Stuffs Act is open to a very wide interpretation, as one definition applies to all manure sold as shoddy, flock dust or wool waste. A shoddy sold as "Best Shoddy" was by no means of high quality, as it only contained 8·6 per cent. of ammonia. The purchaser, however, was given some indication of its manurial value, as it was sold with a warranty of 9·5 per cent. of ammonia.

COMPOSITION OF LIMPETS.—Limpets are to be obtained in considerable quantities on some parts of the coast, and in certain circumstances they are dredged, as they constitute a nuisance. Analyses of wet and dried limpets are as follows:

Water	Nitrogen Per Cent.	Phosphoric acid Per Cent.	Potash Per Cent	Carbonate of lime Per Cent.
70·55	0·40	0·013	—	26·4
4·0	0·54	0·05	0·09	87·1

Dried limpets have, therefore, a distinct manurial value, and form a good source of lime, provided that they are well ground and the shell is finely divided.

F. W. F. ARNAUD

Legal Notes

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

METHYLATED SPIRIT IN SAL VOLATILE

A FIRM of druggists was summoned on February 21st at the North London Police Court for having sold sal volatile, in the preparation of which methylated spirit had been used, and for having used the spirit in the preparation of sal volatile.

Mr. Booth, for the Commissioners of Inland Revenue, said that samples of sal volatile purchased from the defendants contained methyl compounds consistent with the article having been prepared with industrial methylated spirits. The offence was regarded as a serious one, having regard to the toxic effects of methylated spirit.

The solicitor for the defence said that there was reason to believe that an assistant of the company was addicted to sal volatile. The defendants had to answer for the default of this employee, who had since been discharged.

A fine of five pounds on each of the three summonses was imposed, with three guineas costs.

Department of Scientific and Industrial Research

WATER POLLUTION RESEARCH

THE ACTION OF WATER ON LEAD, WITH SPECIAL REFERENCE TO THE SUPPLY OF DRINKING WATER*

THIS Report summarises the information collected from the literature on the subject. It is pointed out in the Introduction that the very different, and sometimes contradictory, conclusions that have been drawn from the results of various investigations are accounted for by the great difficulties involved in any attempt to assess the various factors causing the action of water on lead. These factors include the different gaseous and solid constituents of natural waters, the surface condition of the metal, and the varied susceptibility of individuals to lead poisoning.

The Report deals with these factors under the following headings:

Diagnosis of plumbism—Lead-content of drinking water—Protection of consumers against water plumbism—Instances of lead piping in satisfactory use for long periods—Analytical determination of lead—Action of water on lead—Electrolytic action—Allotropy of lead—Over-voltage—Experimental technique and factors influencing results—"Hard" versus "soft" water—Outbreaks of plumbism and protective measures adopted—Aerated mineral waters—Electrical current leakage and lead contamination—Acidity and its correction—Insoluble substances formed in lead pipes—External attack on lead pipes, cables, etc.—Effects on lead of water and dissolved substances—Summary.

The bibliography (13 pages) contains three hundred and seventy-one references, and there is a name index occupying five pages.

* Technical Paper No. 4. *Summary of Existing Knowledge*, by H. Ingleson, M.A., D.Phil. London: H.M. Stationery Office, pp. 115, 1934. Price 2s. net.

New Zealand

SIXTY-SIXTH ANNUAL REPORT OF THE DOMINION LABORATORY

In his Report for the year 1932 the Dominion Analyst (Mr. W. Donovan, M.Sc., F.I.C.) gives particulars of the chemical analyses and investigations undertaken for the Government Departments. The number of samples examined at the Wellington Laboratory was 5463, and over 2000 samples were analysed at each of the three branch laboratories. Analyses of numerous samples of milk from various parts of the Dominion showed that the quality of the milk is now fairly satisfactory, and in marked contrast with that sold prior to the enforcing of the Sale of Food and Drugs Act.

Identification of Glass Splinters.—A particularly interesting problem, submitted by the Police Department, related to a charge of theft and involved the identification of certain minute splinters of glass. It was shown that the splinters agreed in sp.gr., refractive index, and appearance under ultra-violet light with glass from a broken shop window from which goods had been abstracted, but with no other samples of window or bottle glass that were obtainable.

Manganese Ores and Dry Cell Batteries.—A manganese ore contained 72·0 per cent. of manganese dioxide (≡ 13·3 per cent. of available oxygen), 0·3 per cent. of manganous oxide, 2·3 per cent. of total iron, with less than 0·02 per cent. of nickel and cobalt, together. The specifications for ore for use in the battery trade usually require at least 80 per cent. of manganese dioxide (≡14·72 per cent. of available oxygen), less than 1 per cent. of iron and less than 0·05 per cent. of copper, nickel or cobalt. In addition, physical tests are required; ores with a lower oxygen-content than 14·72 per cent. may be usable if they are sufficiently porous. According to Camp (*Chem. and Metall. Engineering*, March, 1928) the depolarising power of manganese dioxide appears to be not altogether dependent on its MnO_2 content. In different lots of the same type, however, the depolarising quality is directly proportional to the MnO_2 content. Also, Camp regards a proportion of ferric oxide up to 3 or 4 per cent. as harmless, but the presence of metallic iron is very deleterious.

Another manganese ore, from Whangarei, contained 89·6 per cent. of manganese dioxide (≡ 16·5 per cent. of available oxygen), with less than 0·01 per cent. of copper, 1·0 per cent. of total iron, and less than 0·02 per cent. of nickel and cobalt. This was reported as of good quality for chemical use.

Diatomaceous Earth as Filtering Medium.—Two samples from Matamata County gave the following results:—Silica, 83·40, 80·55; loss on ignition, 12·06, 12·42; and residue (chiefly oxides of iron and alumina), by difference, 4·54, 7·03 per cent. Both samples consisted largely of *Melosira*, a small cylindrical form which is the chief form found in many New Zealand diatomites. Associated with it were fairly numerous larger and needle-shaped species, the following being identified: *Cocconema lanceolatum*, *Pinnularia* (very large forms), *Navicula cuspidata*, *Tabellaria* and *Epithemia turgida*. In No. 1 there were present also numerous sponge spicules. No. 2 contained diatoms like those in No. 1, but with a larger proportion of very fine species—*viz.* Diatoma.

With regard to the suitability of the samples for filtration purposes, it is generally considered that the best material is a mixture of diatoms of various shapes, in which those of a thin needle-shaped form predominate. A deposit of diatomaceous earth obtained from California, and said to consist chiefly of a mixture of thin disc-shaped forms (*Coscinodiscus*) and rod-like forms (*Synedra*), together with sponge spicules, is claimed by the owners (The Celite Co., U.S.A.) to be very efficient as a filtering medium. Diatomites, consisting chiefly of the

small cylindrical diatom *Melosira*, are not usually considered suitable for filtration purposes.

Another sample (Rotorua County) was composed chiefly of the diatom *Melosira*, varying little in size. An appreciable quantity of transparent fragmentary glass was also present. The sample could not be recommended as particularly suitable for filtration purposes. Diatomite is used to a considerable extent in the United States and elsewhere as an ingredient in Portland cement concrete to improve workability and resistance to disintegration, especially for marine work. The other major use is for heat, cold, and sound insulation. The sample might find some application in New Zealand along such lines. The presence of the fragments of volcanic glass would detract somewhat from its value as an insulator, but would tend to enhance its value for concrete-making.

TESTS ON ANAESTHETIC CHLOROFORM.—A sample complied with the tests given in the British Pharmacopoeia, 1914, and United States Pharmacopoeia, and also with the more rigid tests recommended by Baskerville and Hamor (*J. Ind. Eng. Chem.*, 1912, **4**).

The resorcinol-vanillin test of Allport (ANALYST, 1931, **56**, 706) gave a slight positive result for hydrochloric acid, indicating incipient decomposition. Allport's test for hydrochloric acid was found to be much more delicate than the silver nitrate test (British and United States Pharmacopoeias), the barium hydroxide test of Baskerville and Hamor, or the benzidine test of the German Pharmacopoeia.

Food Preservatives in Germany*

THE Draft Regulations, published in 1932, are expected shortly to become statutory. Only certain specified substances are permissible as preservatives, and these must comply with the standards of the German Pharmacopoeia. The sale of mixtures of preservatives other than those mixtures appearing in the official list is prohibited, as is also the sale of preservatives mixed with other substances, with the exception of mixtures containing salt, sugar, tartaric acid, citric acid, and mixtures of the ethyl and propyl esters of *p*-hydroxybenzoic acid with sodium carbonate.

Preserved foodstuffs sold in packages must be labelled "chemically preserved," or "chemically preserved with boric acid" when boric acid is present.

The approved preservatives comprise the following, to be used in the amounts specified per 100 grms. of foodstuffs:

Ethyl and Propyl Esters of p-*Hydroxybenzoic Acid including their Sodium Compounds and their Mixtures.*—Fish and crustacean products, 50 mgrms.; salmon, 25 mgrms.; salmon substitute, 25 mgrms.; preserved eggs: liquid egg yolk, 800 mgrms.; margarine, 80 mgrms.; preserved vegetables, pickling liquors, 80 mgrms.; fruit preparations (other than cherry, orange and lemon juices), 90 mgrms.; cherry juice, orange juice, lemon juice, 90 mgrms.; fruit pulp and fruit butters, 90 mgrms.; liquid fruit pectin, 90 mgrms.; non-alcoholic drinks, 50 mgrms.; confectionery, chocolates, 120 mgrms.; ices, 15 mgrms.; coffee extracts and substitutes, 100 mgrms.; malt extract with water-content of 20 to 25 per cent., and in packages of 5 kilos. and over, 50 mgrms.

Hexamethylene-tetramine.—Fish and crustacean products, 25 mgrms., in addition to the above esters (50 mgrms.); fish roes, German roe, caviare, 100 mgrms.; crabs' claws, etc., 50 mgrms.

Hydrogen Peroxide.—Fish in jelly ("Bratmarinaden"), 200 mgrms. in the jelly in addition to the esters (50 mgrms.).

* *Food Manufacture*, 1934, **9**, 102.

Benzoic Acid.—Salmon substitute, 500 mgrms.; crabs' claws, etc., 500 mgrms. (alternative to hexamethylene-tetramine); caviare, 500 mgrms. (alternative to hexamethylene-tetramine); crabs, tinned crabs, 900 mgrms.; preserved eggs: liquid egg yolk, 1000 mgrms., or 1200 mgrms. of sodium benzoate (alternative to the esters; *supra*); margarine, 200 mgrms., or 240 mgrms. of sodium benzoate (alternative to the esters, *supra*); preserved vegetables, pickling liquors, 200 mgrms., or 240 mgrms. of sodium benzoate (alternative to the esters, *supra*); fruit preparations and juices (other than cherry, orange and lemon juice), 180 mgrms. of sodium benzoate (or formic acid, sulphurous acid, potassium sulphite or esters); cherry juice, orange juice, lemon juice, 180 mgrms. of sodium benzoate (or formic acid, sulphurous acid, potassium sulphite or esters); fruit pulp and fruit butters, 150 mgrms. (or 180 mgrms. of sodium benzoate (as alternative); liquid fruit pectin, 180 mgrms. of sodium benzoate; non-alcoholic drinks, 50 mgrms. of sodium benzoate (as alternative); chocolate and confectionery, 150 mgrms. (alternative to esters, *supra*); ices, 100 mgrms. (alternative to esters, *supra*); edible mustard, 150 mgrms.

Boric Acid.—Anchovies, 500 mgrms.; caviare, 500 mgrms. (alternative to hexamethylene-tetramine); crabs: tinned crabs, 900 mgrms.; liquid egg yolk intended exclusively for use in fancy bakeries but not in the production of dietetic foods, 1500 mgrms.

Formic Acid (25 *per cent. Solution*).—Fruit preparations and fruit juices other than cherry, orange and lemon juices, 1000 mgrms. (alternative); cherry, orange and lemon juices, 1600 mgrms. (alternative); liquid fruit pectin, 1000 mgrms. (alternative).

Sulphurous Acid.—Horseradish preparations, 75 mgrms. (as SO_2), or 125 mgrms. of sodium bisulphite; fruit preparations and juices; also cherry, orange and lemon juices, 125 mgrms.; or 435 mgrms. of potassium "pyrosulphite" (alternatives); fruit pulp and fruit butter, 125 mgrms. or 435 mgrms. of potassium "pyrosulphite" (alternatives); fruit juice used directly as a beverage, excepting grape juice, 12·5 mgrms.; dried fruit, 200 mgrms.; edible gelatin, 125 mgrms.

In the preparations of jams, marmalades, etc., benzoic acid, sodium benzoate, formic acid or the esters mentioned above may be used in aqueous or alcoholic solution for wetting parchment paper used as covering for the product packed for sale.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Acid-content of Tomato Purée. G. Mészáros. (*Z. Unters. Lebensm.*, 1934, **67**, 319–321.)—Different brands of tomato purée vary appreciably as regards their acid flavour, the acidity being due, not only to the organic acids occurring in the raw tomatoes, but also to lactic fermentation of the carbohydrates present. To determine the acidity, 50 to 60 grms. of the purée from the middle of the container are thoroughly mixed, and 1 to 2 grms. are weighed out. This is shaken with 70 to 80 ml. of water for 6 to 8 minutes, and the whole is then made up in a measuring flask to 100 ml. and again well shaken. About 15 ml. are then centrifuged, and 10 ml. of the liquid are afterwards titrated with 0·25 *N* sodium hydroxide

solution in presence of phenolphthalein. The result is expressed as ml. of N sodium hydroxide per 100 grms. of purée. For six different brands containing, respectively, 25·6, 26·9, 20·5, 20·3, 7·5, and 9·1 per cent. of dry matter, the acidities found were 30·2, 29·7, 24·6, 18·8, 15·5, and 37·8. The contents of different containers of one and the same brand showed somewhat varying acidities. Determinations of the lactic acid yielded discordant results, although they indicated that the acidity of tomato purée is due mainly to this acid. T. H. P.

Keeping Quality of Frozen Orange Juice. M. A. Joslin and G. L. Marsh. (*Ind. Eng. Chem.*, 1934, **26**, 295–299.)—Frozen orange juice stored at −18° C. deteriorates in flavour when oxygen is present. If the juice is de-aerated previously and stored in an atmosphere of nitrogen, it retains its flavour for months. Flash pasteurisation at about 80° C., with rapid cooling previous to freezing and storage, is also a means of retaining the flavour. W. P. S.

Transition Points of Mixtures of Cow's Butter and Cocoa Butter. D. W. Horn and M. A. Wilson. (*Amer. J. Pharm.*, 1934, **106**, 59–61.)—The transition point of a mixture of fats is found by placing the melted fat in a Dewar test-tube held in the centre of a bath of water and ice. The fat is stirred constantly with a glass stirrer encircling the thermometer inserted in the fat. The temperature is recorded every minute from the time it has dropped to 30° C., and the results are plotted, temperatures vertically and times horizontally; they invariably yield a graph suggestive of the sign $\surd$. Sub-cooling to as much as 5 or 10 degrees may occur before crystallisation sets in accompanied by a gradual rise in temperature. The rise stops at a definite temperature which is held for several minutes, and is called the transition point. A study of mixtures of cow's butter and cocoa butter gave the following observed transition points (agreeing almost exactly with the theoretical values). Percentage of cow's butter 0, transition point, 29·2° C.; 20 per cent., 26·2° C.; 40 per cent., 22·6° C.; 60 per cent., 19·4° C.; 70 per cent., 17·6° C. Up to 70 per cent. of cow's butter there is a linear relation expressed as $y = -0{\cdot}165x + 29{\cdot}2$. The transition point is regarded as useful in factory control, although it is not a substitute for the Reichert–Meissl value.

D. G. H.

Adulteration of Cocoa Butter. Determination of the "Azelaic Acid" Values of Palm and Illipé Butters. G. Schuster. (*J. Pharm. Chim.*, 1934, **126**, 206–209.)—The procedure previously described (ANALYST, 1933, **58**, 763) may be simplified as follows:—After oxidation, the insoluble brown mass (potassium salts of azelaic glycerides mixed with manganese dioxide) filtered off is dried in a vacuum over sulphuric acid to expel all traces of acetone. The powder thus obtained is extracted for about 30 minutes in a Soxhlet apparatus with boiling alcohol (7 to 8 times the weight of the original fat). The potassium salts of the azelaic glycerides and the pelargonate dissolve in the alcohol, a small amount of which is oxidised to acetaldehyde by the excess of permanganate remaining in the dried mass. The hot alcoholic solution is treated with excess of concentrated magnesium chloride solution at the same temperature. The subsequent operations are as already described (*loc. cit.*). The mean azelaic acid value was 121·1 for illipé butter, and 132·8 for palm butter. T. H. P.

Gadoleic Acid in Cod-liver Oil. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 14–17B.)—The methyl esters (3000 grms.), resulting from the action of methanol on the oil at room temperature in the presence of potassium hydroxide, were fractionated, and the lithium salts of the fatty acids, liberated from the fraction of b.pt. 210° to 225° C. at 10 mm. pressure (yield 594 grms.) were extracted with 50 per cent. alcohol. The insoluble portion (mainly salts of mono-ethylenic acids with some derived from saturated acids) was acidified with hydrochloric acid, the acids being distilled as methyl esters, and the fraction (59 grms.) of b.pt. 217° to 221° C. at 10 mm. pressure was treated by the lead salt and alcohol method with a quantity of lead acetate equivalent to about 10 per cent. of the fatty acids. The unsaturated acids in solution were recovered by evaporation and purified by repeated re-crystallisation from 80 per cent. alcohol, when gadoleic acid was obtained in needles, having sp.gr. at 25°/4° C., 0·8882; n_D^{25}, 1·4597; m.pt., 24° to 24·5° C.; neutralisation value, 179·9; and iodine value, 81·0. On hydrogenation they yielded arachidic acid, the identity of which was established by the mixed melting-point method. The colourless syrupy ozonide remaining after passing ozonised oxygen through a solution of 4 grms. of the acid in 40 ml. of chloroform and evaporating, was decomposed in 40 ml. of boiling water, and the cool solution was extracted with 400 ml. of ether, which were evaporated. The new residue was then extracted 3 times with 40 ml. of hot petroleum spirit, the solid which separated on cooling being added to the other insoluble matter (total 1·3 grm.). (*a*) The solution obtained at this stage yielded 1·7 grms. of colourless distillate when distilled under 100 mm. pressure at temperatures up to 215° C., and this was mixed with a slight excess of potassium carbonate solution and shaken with ether in order to separate the neutral matter, the acidic portion being liberated from the soap solution and re-crystallised from 60 per cent. alcohol (neutralisation value, 300·1; m.pt., 27° C.). This was identified with undecanoic acid by the mixed m.pt. method, in which the acid prepared by hydrogenation of undecenoic acid obtained by dry distillation of castor oil was used. The neutral substance in the ether gave Schiff's reaction for aldehydes. The residue from distillation was treated with an alkaline solution of potassium permanganate, and the residue left after evaporation of an extract of the oxidation products in ether was extracted with hot water. A crystalline solid (neutralisation value, 592·0; m.pt., 102° to 103° C.) was deposited from the cool solution, and was probably impure azelaic acid. (*b*) An extract in hot water of the white residue insoluble in petroleum spirit was oxidised with potassium permanganate, and the liquid was extracted with ether. This removed a substance which was shown (by the mixed melting-point method) to be azelaic acid. It was then deduced that the constitution of gadoleic acid is

$$CH_3(CH_2)_9\,CH{:}CH(CH_2)_7.\,COOH,$$

namely, the same as that given by Takano (*id.*, 1933, **36**, 131) for the eicosenoic acid from Japanese sardine oil, and the identity of the two acids is therefore established (see also, Toyama, *id.*, 1925, **28**, 95; 1926, **29**, 531, 538; 1927, **30**, 63, 116, 207, 519; ANALYST, 1927, **52**, 245; Tsujimoto, *id.*, 1926, **51**, 49; Hilditch and Lovern, *id.*, 1928, **53**, 352; and also following abstract).

J. G.

Identification of Gadoleic Acid in Japanese Sardine Oil, Herring Oil and Liver Oil of "Sukeso-Dara" (*Theragra Chalcogramma*). Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 17–20B.)—The methods used were essentially the same in principle as those described in the preceding abstract, exceptions being indicated below. In the case of Japanese sardine oil the fraction (b.pt. above 215° C., at 10 mm. pressure) of the ethyl esters obtained by ethanolysis of the oil, was treated by the sodium salt and acetone method, the fatty acids liberated from the insoluble sodium salts being converted into the methyl esters which, when distilled, gave a fraction of b.pt. 218 to 225° C. (at 10 mm.). The lithium salts of the acids of this fraction which were insoluble in 50 per cent. alcohol were then separated and decomposed by acid, and were treated by the lead salt and alcohol method, as before (*loc. cit.*), the unsaturated acids being again converted into the methyl esters. The fatty acids from the fractionation of these (b.pt. 217° to 221° C., at 10 mm.) were again purified by the lithium salt process to remove the last traces of highly-unsaturated acids, and pure gadoleic acid was finally obtained by repeated re-crystallisation, from 80 per cent. alcohol of the acids from the insoluble lithium salts. Hydrogenation of the gadoleic acid gave arachidic acid; oxidation by Hazura's method gave a dihydroxy-arachidic acid in lustrous leaflets, m.pt. 128° to 128·5° C.; and the elaidin reaction gave a product of m.pt. 51·5° to 52° C. Ozonisation was then applied, as described before (*loc. cit.*), and the production of undecanoic and azelaic acids confirmed the structure of gadoleic acid already deduced. Herring oil and the liver oil of "sukeso-dara" were investigated in a similar way, and with the same final result. In the latter case the acid was not examined by ozonisation, although its identity was confirmed by the mixed melting-point obtained with gadoleic acid from cod-liver oil. The values of the original liver oil were:—sp.gr. at 15°/4° C., 0·9231; n_D^{15} 1·4798; acid value, 2·4; saponification value, 183·3; iodine value, 150·1; unsaponifiable matter, 0·92 per cent. J. G.

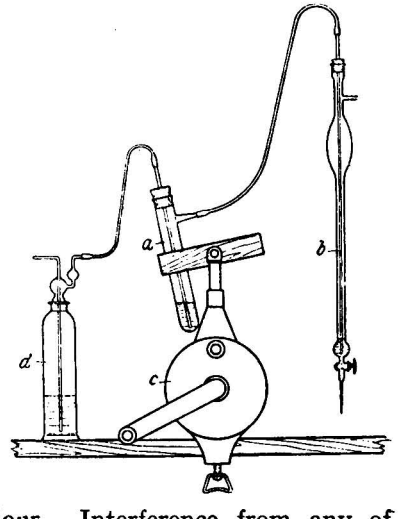
Fatty Substances of Shell-Fish. M. Tsujimoto and H. Koyanagi. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 81B.)—I. *Shell-Fish in the Group Pelecypoda.*—The fatty matter amounts to about 0·7 per cent. of the undried fish (free from shell). Of this amount, more than half consists of phosphatides, the fatty acids of which have high iodine values. Unsaponifiable matter may reach 45 per cent. It contains a peculiar sterol which forms an acetate of high m.pt., and shows a characteristic red colour reaction in acetic anhydride solution when a drop of strong sulphuric acid is applied. The author considers that this sterol may be identical with clionasterol (Dorée, *Biochem. J.*, 1909, **92**).

II. *Shell-Fish in the Group Gasteropoda.*—The fatty matter amounted to 1 per cent., and the phosphatides to about 40 per cent. for ear-shell (*Haliotis gigantea*), and about 61 per cent. for top shell (*Turbo cornutus*). The unsaponifiable matter was about 20 per cent. and 38 per cent., respectively. It consisted chiefly of cholesterol, but also contained some of the more uncommon sterol found in the *Pelecypoda*. R. F. I.

Constituents of Menuke Oil. S. Ueno and M. Iwai. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 52B.)—The menuke fish, which belongs to the family

Scorpaenidae, is found in the Sea of Japan. The oil is orange-yellow, and has an odour similar to that of herring or shark oil. The specimen examined had the following constants:—Sp.gr. at 20/4° C., 0·9155; n_D^{20}, 1·4721; acid value, 2·83; saponification value, 181·8; iodine value, 107·2; Reichert–Meissl value, 0·51; unsaponifiable matter, 1·40 per cent. By the lead salt and ether process 12 per cent. of solid fatty acids and 88 per cent. of liquid fatty acids were found. The solid fatty acids contained 70 per cent. of palmitic acid and relatively small amounts of stearic and myristic acids. The liquid fatty acids belonged chiefly to the oleic acid series, and contained oleic (chiefly), with smaller amounts of the acids $C_{16}H_{30}O_2$, $C_{20}H_{38}O_2$ and $C_{22}H_{42}O_2$. In the more unsaturated series clupanodonic acid was the chief constituent. R. F. I.

Auto-oxidative Rancidity of Fats. VI. Technique and Evaluation of the Kreis Reaction. K. Täufel and P. Sadler. (*Z. Unters. Lebensm.*, 1934, **67**, 268–273.)—The Kreis reaction of fats depends on the formation of epihydrinaldehyde owing to auto-oxidation of the fatty material. Fats may undergo degradation in other ways, and in such cases the Kreis reaction fails. As auto-oxidation proceeds, the proportion of epihydrinaldehyde increases to a certain point, but, finally, it may become constant or even diminish. Strict parallelism between the intensity of the Kreis reaction and the extent to which auto-oxidation has proceeded cannot, therefore, be expected. This reaction is usually carried out by shaking the oil or melted fat with concentrated hydrochloric acid and adding a solution of phloroglucinol in ether. Such procedure renders the reaction liable to disturbance from various causes. For instance, red colours are yielded by a number of substances, including allyl alcohol, allylamine, diallylcarbamide, eugenol, etc. Moreover, if the aldehyde concentration has greatly increased owing to advanced deterioration of the fat, sparingly soluble, colourless aldehyde phloroglucides are formed, the Kreis colour reaction being prevented. Difficulty may also arise if the product being tested has appreciable colour. Interference from any of these causes is avoided by either of the two following alternative procedures.



(i) *Cotton-wool Plug Method.*—The oil or carefully-melted fat is mixed in a short test-tube with an equal quantity of concentrated hydrochloric acid (ice-cooled). A cotton-wool plug, inserted in the tube at its upper dry part, is moistened with about 1 ml. of 0·1 per cent. solution of phloroglucinol in alcohol and 10 drops of hydrochloric acid (at least 20 per cent.). The tube is well shaken for 1 to 2 minutes without splashing the cotton, and may, if necessary, be gently heated (to about 40° C.). Red coloration of the lower surface of the plug indicates epihydrinaldehyde. (ii) *Crucible Method.*—The test-tube is replaced by a tall porcelain crucible covered with filter-paper kept moistened with the reagent.

To obtain an approximately quantitative measure of the epihydrinaldehyde, use is made of the apparatus shown in the figure. From 2 to 3 ml. of the oil, and the same volume of concentrated hydrochloric acid, both ice-cold, are placed in *a*, which is immersed in ice-water, and is connected with a gas-washing bottle, *d*, and an absorption tube, *b*, containing, in its lower bulb, an ice-cooled mixture (1 : 1) of the alcoholic 0·1 per cent. phloroglucinol solution and concentrated hydrochloric acid. A stream of air, sufficiently rapid to force the reagent into the upper bulb of the absorption tube, is drawn through the apparatus. Liberation of the epihydrinaldehyde may be accelerated by shaking the tube *a*, and is then usually complete in 30 minutes. If a phloroglucide precipitate appears in *b*, the test must be repeated with a smaller quantity of the oil. When a solid fat is to be tested, gentle warming of *a* becomes necessary, but the temperature should be kept as low as possible. The contents of the absorption tube are compared in a colorimeter with standard tubes prepared with known amounts of epihydrinaldehyde. This procedure does not affect glycerides, but, when it is applied to free linolic acid, epihydrinaldehyde is gradually formed, owing to oxidation of the acid by the oxygen of the air-current. Danger of such oxidation is avoided by replacing the stream of air by one of nitrogen or carbon dioxide. (*Cf.* Täufel, ANALYST, 1931, **56**, 541.) T. H. P.

Photochemical Studies of Rancidity. N. R. Coe and J. A. Le Clerc. (*Ind. Eng. Chem.*, 1934, **26**, 245–248.)—Colour tests for rancidity and the peroxide test for the decomposition of an oil may not indicate conclusively that an oil is rancid, and these tests are not reliable when applied to oils which have been protected from light. Oils protected from light by opaque black paper, or by green paper transmitting light delimited by 490$m\mu$ to 580$m\mu$, remain free from rancidity even after seven months, although they give strong positive tests with both the Kreis and the von Fellenberg reagents, and have peroxide values equal to, or higher than, that of an unprotected oil which has become rancid. Similar results are obtained when air has been bubbled through the oils at the rate of 6 litres per hour. Oxidation rancidity appears to be due to photochemical action on a compound which probably exists simultaneously in the oil, or is produced from compounds which give rise to the formation of peroxides.

W. P. S.

Photochemistry of Cod-liver Oil. J. H. Graham. (*Amer. J. Pharm.*, 1934, **106**, 44–56.)—It has been found that the golden-yellow fluorescence of cod-liver oil exposed to light of sufficient intensity disappears in about 90 days, leaving a pale yellow or almost colourless oil. At the same time, the pink colour of the Kreis test, given at first with all the four oils used, develops more quickly with the lapse of time, giving rise to a faint purple, or, with specimens kept in the dark, to a deep red colour. However, the Hagar–Salkowski reaction is regarded as more conclusive in determining the effects of light exposure and rancidity (that is, the relative freshness of the oil), than the apparently more delicate Kreis test. In the former test a violet or purple colour, changing slowly to brown on the addition of one drop of concentrated sulphuric acid to a solution of one drop of oil in one ml. of chloroform, indicates possible freedom from rancidity.

In the oils kept for 90 days the formation of the purple colour was gradually replaced by the immediate development of the brown colour, followed by a brown precipitate. No consistent correlation was found between saponification, iodine, and free acid values, and variations of air, moisture, light and temperature conditions seem to preclude it. The chemical complexity of cod-liver oil is emphasised; important chemical changes take place rapidly if proper conditions are not maintained, such as exclusion of excessive moisture, light and air, and the maintenance of comparatively low and uniform temperatures. D. G. H.

Analytical Constants of Peanut Butter. H. L. Wikoff, M. Busey and A. M. Kaplan. (*Ind. Eng. Chem.*, 1934, **26**, 291–292.)—Peanut butter consists of the finely-ground whole nuts. Ten different brands contained from 0·8 to 3·7 per cent. of moisture, and the dry samples yielded:—Ash, 1·91 to 3·18; acid-insoluble ash, 0·07 to 0·25; oil, 39·45 to 52·34 per cent. The dry, oil-free meals contained:—Proteins, 54·64 to 62·45; sodium chloride, 1·08 to 3·45; total reducing substances, expressed as dextrose, 22·77 to 29·92; crude fibre, 2·67 to 4·31; starch, 14·46 to 21·43; pentosans, 5·30 to 6·81 per cent. The variation in the amount of chloride is due to the fact that common salt is added as a seasoning agent.

W. P. S.

Assay of Strychnine Alkaloid in Strychnine Sulphate Tablets. F. J. Amrhein. (*Amer. J. Pharm.*, 1934, **106**, 57–58.)—The official method of the A.O.A.C. for the determination of strychnine in tablets takes no account of the presence of interfering fillers or of mineral oil added as a lubricant in the manufacture. To overcome error due to these sources, the following modified method is advocated:—The tablets (25 to 100) are weighed and placed in a separating funnel, and 20 ml. of water and 1·2 ml. of 10 per cent. sulphuric acid are added. After complete disintegration, two extractions are made with 25-ml. portions of chloroform; the liquid is then made alkaline with ammonia water (1+2), and five extractions are made with 25, 20, 15, 10, and 5 ml., respectively, of chloroform, or until the alkaloid is completely removed. The first two extracts are placed in a separating funnel plugged in the stem with absorbent cotton wet with chloroform, and washed with 5 ml. of water containing a drop of the dilute ammonia. The clear chloroform layer is removed, and each successive chloroform extract is washed with the same wash water and filtered, the outside of the funnel stem being also finally washed with chloroform, which is added to the main portion. The combined extracts are evaporated on a steam bath, but the drying of the final 3 to 5 ml. is finished in a current of air. Two to 3 ml. of neutral alcohol are added, the mixture is warmed, and the solution is titrated with 0·02 *N* acid (methyl red as indicator) until a faint pink tint appears, when 50 ml. of boiled water are added, and the titration is continued to a faint red end-point. One ml. of 0·02 *N* acid is equivalent to 6·684 mgrm. of strychnine. With 1/40 grain tablets the method gave 1/40 grain of strychnine, and, with 1/60 grain tablets, 1/60 grain, whereas the regular A.O.A.C. method gave results for 1/40 grain tablets varying from 1/48 to 1/50 grain, and 1/60 grain tablets were returned as 1/90 grain.

D. G. H.

[Hydrocyanic Acid in] Tobacco Smoke. IV. E. Waser and M. Stähli. (*Z. Unters. Lebensm.*, 1934, **67**, 280–284.)—The method used for determining the content of hydrocyanic acid in cigarette smoke was a modification of that used by Lehmann and Gundermann (*Arch. Hyg.*, 1912, **76**, 98) for cigar smoke. The smoke was washed with dilute sulphuric acid to remove tarry constituents, filtered through cotton wool, and passed into a definite volume of standard silver nitrate solution containing nitric acid, distributed between three absorption flasks. The silver cyanide (always found free from thiocyanate) thus formed was converted, by addition of ammonia solution, into silver ammonium cyanide. The solution thus obtained is clear and colourless, so that purification with animal charcoal, which might result in some adsorption of the double cyanide, is unnecessary. By dropwise addition of concentrated nitric acid, silver cyanide was precipitated and, after removal of this by filtration, the residual silver in the solution was determined by titration with standard ammonium thiocyanate solution. The proportion of hydrogen cyanide in the smoke from cigarettes of various kinds was found to vary between 0·020 and 0·034 per cent. of the dry matter of the tobacco smoked. The amount found is independent of the nicotine-content of the tobacco and, for any one type of cigarette, is constant under constant conditions of smoking, although it increases with the rapidity of smoking. The amounts of hydrogen cyanide found are considered too small to constitute any direct danger to the smoker. T. H. P.

Determination of Arsenic in Medicinal Organic Compounds. E. Kahane. (*J. Pharm. Chim.*, 1934, **19**, 116–123.)—*Destruction of Organic Matter.*—To a sample of the compound weighting 0·2 to 0·4 grm. are added 5 ml. of an acid mixture containing 700 ml. of concentrated sulphuric acid, 100 ml. of concentrated nitric acid and 200 ml. of perchloric acid (sp.gr. 1·61), and the whole is heated until fumes of sulphuric acid are given off; the addition of a few drops of a mixture of 2 vols. of perchloric acid and 1 vol. of nitric acid, and further heating, may be necessary to produce a colourless liquid. The arsenic in the solution is present in the quinquevalent form. *Determination of Arsenic.*—Whilst many of the usual methods are applicable, the following modification of the bromate process is preferred:—To the colourless sulphuric acid liquid, about 0·25 grm. of hydrazine sulphate crystals is added, and the liquid is heated for 10 minutes in order to reduce the arsenic to the tervalent form, and to decompose the excess of the reducing agent. The solution is cooled before and after the addition of 20 ml. of water, 0·1 to 0·2 grm. of potassium bromide is added, and the solution is titrated with standard potassium bromate solution until a faint yellow colour (due to free bromine) appears; this is stated to afford a more sensitive indication of the end-point than the more usual expedient involving the bleaching action of the free bromine on an added dye, *e.g.* methyl orange; 1 ml. of 0·1 *N* potassium bromate solution ≡ 3·75 mgrms. of arsenic. Good results were obtained with a wide range of organic arsenic compounds. S. G. C.

Biochemical

Heavy Water Content of the Water in Milk. H. Erlenmeyer and H. Gärbner. (*Helv. Chim. Acta*, 1934, **17**, 334.)—The authors have previously described (*Helv. Chim. Acta*, 1934, **17**, 30) an apparatus with lead electrodes, by means of which the electrolytic decomposition of 8 litres of ordinary pure water yielded 20 ml. of heavy water of sp.gr. 1·00087. In view of biological differences in the effects of ordinary water and heavy water, the experiment was repeated on 8 litres of the water obtained from milk of undoubted purity. This also yielded 20 ml. of heavy water of sp.gr. 1·000832, and the conclusion is, therefore, drawn that the water of milk has the same composition as ordinary water, and that the biological filtration of the water in the process of the formation of milk does not lead to an increase in the proportion of the toxic heavy water.

Colorimetric Method for Determination of Glucosamine and Chondrosamine. L. A. Elson and W. T. J. Morgan. (*Biochem. J.*, 1933, **27**, 1824–1828.)—These substances are heated in alkaline solution with acetylacetone, and thus converted into pyrrole derivatives, which, on treatment with Ehrlich's reagent (*p*-dimethylaminobenzaldehyde in acid solution) in the presence of alcohol, give rise to very stable red solutions. Results show that the error of determination is less than 5 per cent. if the amount of glucosamine hydrochloride is within the range 0·75 to 3·0 mgrm., and if the colour intensity of the standard glucosamine hydrochloride solution does not differ by more than 25 per cent. from that of the unknown. Equal amounts of glucosamine hydrochloride and chondrosamine hydrochloride give rise to colours identical in tint and intensity. Under the specified conditions the accuracy of the determination is not affected by the presence of glucose, galactose, fructose, arabinose, glycine, alanine or histidine; tryptophane has no effect, as the tryptophane reaction with Ehrlich's reagent requires a greater concentration of acid. Many carbohydrates and amino-acids also interfere in more highly acid solutions. Although 1-aminoglucose is not known to occur naturally, and is, therefore, unlikely to be present in the products of the acid hydrolysis of either gluco-proteins or nitrogen-containing polysaccharides, this aminohexose condenses readily with acetylacetone, and, under the experimental conditions described for glucosamine and chondrosamine, yields a coloured solution almost identical in tint and intensity with that produced by equal quantities of these compounds. The new method is more satisfactory than the colorimetric method for the determination of glucosamine recently described by Zuckerkandl and Messiner–Klebermass (*Biochem. Z.*, 1931, **236**, 19), since it avoids the process of evaporation to dryness and subsequent conversion of the glucosamine into its *N*-monoacetyl derivative. P. H. P.

Colorimetric Determination of Vitamin *A* by the Alkali Digestion Method. A. W. Davies. (*Biochem. J.*, 1933, **27**, 1770–1774.)—A simplified form of the alkali digestion process for the assay of vitamin *A* in tissues by the colorimetric method has been devised. The method was first adopted by Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 111), and was used upon samples of human liver obtained at autopsy by Moore (*Lancet*, 1932, ii, 669). The new process

permits of rapid working (it is possible to average 3 to 4 assays per hour), and gives results substantially in agreement with those obtained by the Soxhlet extraction method. The digest is given a preliminary shaking with a small proportion of alcohol, and then a single extraction with ether is sufficient to extract almost all (usually 90 per cent. or more) of the vitamin *A*. Two washings of the ethereal extract are sufficient to secure freedom from alkali, and, by adherence to the correct proportions of alcohol, ether and water, the formation of emulsions can be avoided except in rare instances. Details of the method are given. The effect of ageing on the stability of the vitamin has been studied, not with a view to ascertaining the ideal conditions for ensuring its stability, but in order to obtain information as to its behaviour under routine conditions involving periods of storage at ordinary temperatures, *e.g.* during transmission by post. It was found that at room temperature vitamin *A* deteriorates less rapidly in liver specimens treated with potash than in untreated tissues kept without preservative treatment. In the case of specimens of liver transferred immediately *post mortem* to potash solution, and then stored at room temperature, no serious decrease in vitamin *A* content is to be anticipated if the assay is carried out within 14 days of death.

P. H. P.

Grouping of Halibut Liver Oils. R. T. M. Haines and J. C. Drummond. (*J. Soc. Chem. Ind.*, 1934, **53**, 81–82T.)—An extensive range of halibut liver-oils of known origin were examined shortly after their preparation, particularly in respect of their vitamin *A* "blue" values (calculated to refer to 0·2 ml. of a 10 per cent. solution) and iodine values. Previously the smaller range of oils examined were of very uncertain origin, and no obvious correlation was found in which the vitamin-content was concerned (ANALYST, 1933, **58**, 356). The iodine values were determined by the method originally described by Rosenmund and Kuhnhenn, using pyridine sulphate bromide as halogenating agent. The oils were from three districts, West Greenland, "Labrador," and East Greenland and Faröe. When the iodine values were plotted against the blue values, the points representing West Greenland oils fell on a smooth curve, and in cases where the vitamin *A* values were below about 2000 blue units the graph was sensibly a straight line, curvature becoming apparent only when the actual bulk of vitamin was appreciable. Since the range of blue values of the "Labrador" (*a*) and East Greenland and Faröe oils (*b*) was limited, (*a*) 325 to 730, and (*b*) 558 to 1700, the effect for these oils was not so striking, but in each case the points were grouped about a line. Iodine values corresponding to zero blue values were 112·5 for West Greenland, and 123·25 for Faröe oils, and it is suggested that East Greenland and Faröe oils are distinguished from West Greenland oils by their higher values for the ratio iodine value/blue value, at least for the 1933 season. The range of blue values for West Greenland oils was 523 to 4350, and iodine values 116·9 to 161·0; for "Labrador" oils, 325 to 730 and 116·2 to 121·5; and for East Greenland and Faröe oils 558 to 1700 and 124·5 to 135. A further examination of a Danish, 2 Norwegian and 4 American oils gave figures so completely different (except in one case) from those for the authentic samples, that blending of cod-liver oils and halibut oil was suspected and a table is given showing the blue and iodine values for various mixtures of this kind.

D. G. H.

Standardisation of the Antiscorbutic Potency of Ascorbic Acid. L. J. Harris and S. N. Ray. (*Biochem. J.*, 1933, **27**, 2016–2021.)—Results are published which confirm conclusions given in an earlier note by Harris and Ray (ANALYST, 1933, **58**, 489). Assays by the tooth protection method, on large numbers of guinea-pigs, and with ascorbic acid and orange juice always given simultaneously at various identical levels of potency, show consistently that the activity is such that 2 mgrms. of ascorbic acid are equivalent to 3 ml. of orange juice, or, that the minimum dose for full tooth protection (under the conditions of the test) is 2 mgrms. This value agrees with the amount of ascorbic acid actually present in average specimens of orange juice, or in "good" lemon juice, as determined by titration (0·6 to 0·7 mgrm. per ml.). The authors state that their use of orange juice as a secondary or derived standard, in place of lemon juice used direct as primary standard, may be criticised, but they believe it to have some advantages. Lemon juice is subject to some variation in potency, so that the evaluation of ascorbic acid in terms of International Units will depend on the quality of the lemon juice used for comparison, but, taking the interpretation that the standard lemon juice means a "good" specimen, equivalent to the orange juice used in the test, and showing 0·6 to 0·7 mgrm. of ascorbic acid per ml. on titration, ascorbic acid has a potency of 15 International Units per mgrm. Against "average" lemon juice as purchased retail in Cambridge, having an ascorbic acid content of 0·47 mgrm. per ml., the calculated activity for ascorbic acid works out rather higher, *viz.* 21 International Units per mgrm. The alternative value, 7·4 units per mgrm., put forward by Key and Morgan (*Biochem. J.*, 1933, **27**, 1030), would indicate an ascorbic acid-content of 1·35 mgrms. per ml. for lemon juice, which seems difficult to reconcile with the fact that the reducing titre rarely rises above a value equivalent to about 0·7 mgrm. Possible reasons for the lack of agreement are discussed. The earlier conclusion of the authors is confirmed, *viz.* that lemon juice is an unsatisfactory standard, and should be replaced by ascorbic acid. Different specimens of lemon juice had ascorbic acid contents varying from 0·19 to 0·69 mgrm. per ml.; average 0·47, with an average deviation of ±0·11. P. H. P.

Indophenol-Reducing Capacity and Vitamin *C* Content of Extracts of Young Germinated Peas. S. W. Johnson. (*Biochem. J.*, 1933, **27**, 1942–1949.)—It has been known for a considerable period that, whilst many dried seeds are devoid of antiscorbutic activity, they acquire this property very readily on germination. Experiments were undertaken to ascertain whether a quantitative relationship exists between the indophenol-reducing capacity and antiscorbutic activity of extracts of peas in the early stages of germination, and, also, if no such relationship exists, whether this is due to the presence of an active oxidised form of the vitamin in the young seedling. A number of extracts were prepared from peas germinated for 3 days, and both their indophenol-reducing capacities and their antiscorbutic activities were determined. The extracts with even the highest indophenol-reducing capacity were found to possess only half the antiscorbutic activity of the germinated peas from which they were obtained. Aqueous, phosphate and cyanide-phosphate extracts were found to be less active antiscorbutically

than would have been expected if their indophenol-reducing capacity had been entirely due to ascorbic acid. All extracts from the germinated peas contained at least one substance other than ascorbic acid which reduced indophenol. No evidence was obtained that the active oxidised form of the vitamin was present in the early stages of germination. The ungerminated peas, which showed no antiscorbutic activity when tested in quantities of 2·5 grms., gave extracts which also reduced indophenol, though at a rather slower rate than ascorbic acid. It is evident, therefore, that the indophenol-reducing capacity of extracts is no true index of the antiscorbutic potency of the seedlings from which they were obtained, and that the formation of the active oxidised form of the vitamin during the early stages of germination is unlikely; it seems that the activity of the peas is due entirely to the reduced form of the vitamin. The fact that the extracts were less active than the peas from which they were prepared can best be explained on the grounds that it is not possible, by the methods used, to extract the vitamin completely. This shows the ease with which misleading results may accrue from testing extracts instead of tissues. If a part of the vitamin is bound to inhibiting substances, as suggested by Euler, it would seem most probable that such a complex would be insoluble or otherwise inextractable. P. H. P.

Vitamin *C* Content of Canned Tomato Juice. R. G. Daggs and A. G. Eaton. (*Ind. Eng. Chem.*, 1934, **26**, 292–295.)—The vitamin *C* content of commercial tinned tomato juice, estimated by Höjer's method of examining sections of the teeth (*Brit. J. Exptl. Path.*, 1926, **7**, 356), is only very slightly lower than that of the fresh juice. W. P. S.

Reactions of Terpenes with Antimony Trichloride. V. E. Levine and E. Richman. (*Biochem. J.*, 1933, **27**, 2051–2054.)—Various workers have shown that antimony trichloride in chloroform solution yields colour reactions with fish-liver oils and fish-liver oil concentrates, with carotenoid pigments, with certain sterols and their derivatives, and with certain five-membered monoheterocyclic compounds. Since unsaturation and the terpene groupings are common chemical factors in carotenoid pigments, in vitamin *A* and in sterols occurring in the plant and animal organism, the authors have studied the antimony trichloride reaction (Carr and Price reagent) on over thirty compounds of the terpene group. The reagent was tested on solutions of the terpenes in chloroform, and also on solutions of the terpenes in chloroform to which acetic anhydride had been added; the acetic anhydride prevents the formation of precipitates in the reaction mixture, and induces a more vigorous reaction and a more intense display of colour changes. The results, which are tabulated, show that the reaction is usually characterised by a succession of colour changes; in many cases the final colour is purple. Citral, in the presence of acetic anhydride, changes from dark yellow to brown, to wine red, to purple and, finally, to dark blue. Ionone, which may be obtained by the oxidation of carotene and of vitamin *A*, gives with antimony trichloride an amber colour changing to wine-red, and, finally, on long standing, to purple. In the presence of acetic anhydride the initial colour is amber, which changes to greenish-amber, mahogany-brown, and, finally, to reddish purple. Vogel and Stohl (*Ber.*, 1933, **66B**, 1066) converted β-ionone by cyclisation with sulphuric

acid into an orange-yellow powder, which gave with antimony trichloride in chloroform solution a permanent and very intense blue colour with a maximum absorption spectrum at 510$m\mu$, and a large band beginning at 430$m\mu$. The following compounds yield no colour reactions: *dl*-camphor, *d*-camphoric acid, *d*-camphoric anhydride, *d*-camphorsulphonic acid and *l*-menthol. The following react very slowly and very slightly: *d*-camphor, borneol and *l*-menthone. The terpenes that react most vigorously are the unsaturated ones, and the higher the degree of unsaturation, the greater the reactivity of the compound. The presence of an aldehyde, alcohol or ketone group induces greater reactivity in the unsaturated compound. The camphane group is the least reactive, and the olefine group the most reactive. P. H. P.

Agricultural

Rapid Determination of Small Quantities of Lime in Soil Solutions. H. Beutelspacher. (*Z. anal. Chem.*, 1934, **96**, 161–172.)—The process is based upon the precipitation of calcium by a known amount of sodium tungstate and colorimetric determination of the excess of tungstate with titanous chloride. One ml. of solution (maximum content, 0·16 mgrm. CaO) is treated in a basin with 1 ml. of sodium tungstate solution (1·0487 grm. per litre; 1 ml. ≡ 0·2 mgrm. CaO), and evaporated to dryness on a water-bath. The residue is extracted with 2 ml. of distilled water; the insoluble part is rubbed and detached with a rubber-tipped glass rod, and the whole is transferred to a pointed tube and centrifuged for several minutes. One ml. of clear supernatant solution is transferred to a small tube and treated first with 0·2 ml. of 0·1 *N* hydrochloric acid, then with 1 ml. of titanous chloride solution (1 ml. of this is equivalent to 2 mgrms. of iron, as determined by titration of a standard ferric chloride solution in presence of thiocyanate). The blue colour can be matched at once against that produced by titanous chloride in the standard tungstate solution. Standard and assay should not deviate more than 30 per cent. The colour is stable for 2 to 3 hours; 50 determinations can be carried out together in about 2 hours. The normal inorganic constituents of soil solutions do not interfere. W. R. S.

Organic Analysis

Determination of Formaldehyde and Sulphites by Acidimetry. M. Malaprade. (*Compt. rend.*, 1934, **198**, 1037–1039.)—Since a rapid reaction occurs between formaldehyde and a neutral sulphite when one or other is present in excess, and the resulting formol-bisulphite combination is neutral in the presence of phenolphthalein and thymolphthalein, either substance may be determined by titrating the liberated sodium hydroxide. Thymolphthalein changes from colourless to blue at a p_H of 9·5 to 10·5. *Formaldehyde.*—The sample is first neutralised to the turning point of thymolphthalein, an excess of a neutral solution of sulphite (prepared by neutralising a solution of bisulphite) is then added, and the liberated sodium hydroxide is titrated until the indicator becomes colourless. It is not necessary to exclude air. *Sulphite.*—The sample is neutralised as before (but out of contact with air), excess of formaldehyde solution

is added (itself first neutralised), and the liberated sodium hydroxide is titrated in air until the indicator is colourless, when phenolphthalein is added, and the titration is continued until the solution is colourless. It is possible thus to determine sulphites in the presence of hyposulphites, which have no action on formol, and also the free sulphur in rongalite. The titration of free alkali may conveniently be carried out with acetic acid containing sodium acetate, in order to eliminate local reactions due to the presence of strong acids. D. G. H.

Determination of Hydroxyl Groups in Alcohols and Phenols by Benzoylation in Tetrahydronaphthalene Solution at High Temperatures. T. M. Meijer. (*Rec. Trav. Chim. Pays-Bas*, 1934, **53**, 387–397.)—This method is based on determination of the hydrochloric acid liberated when an alcohol or phenol is treated with benzoyl chloride or one of the nitrobenzoyl chlorides. Tetrahydronaphthalene is used as a solvent for the reacting compounds, as its high boiling-point (205° C.) renders the use of sealed tubes unnecessary. A stream of air or hydrogen, free from carbon dioxide, is passed through a wash-bottle containing sulphuric acid, and then through the solution of alcohol (or phenol) and benzoyl chloride contained in a flask heated in an oil-bath. The gas proceeds upwards through a reflux condenser, and then through an absorption bottle containing water and afterwards through another charged with silver nitrate solution. The contents of the first of these absorption bottles are afterwards titrated with 0·1 *N* sodium hydroxide solution in presence of methyl red.

When benzoyl chloride was used, the percentages of the theoretical amounts of hydrogen chloride liberated from different hydroxyl compounds were: resorcinol, 94; quinol, 90·6; catechol, 84·6; benzyl alcohol, 90·4; cyclohexanol, 103·3; benzoin, 101·3; propyl alcohol, 84; isopropyl alcohol, 100; glycol, 62; glycerol, 48·2. With *p*-nitrobenzoyl chloride, the figures were: phenol, 101·6; β-naphthol, 94·9; resorcinol, 91·3; quinol, 92·3; catechol, 74; benzyl alcohol, 102·3; benzoin, 88·3; cyclohexanol, 101; 1 : 2-methylcyclohexanol, 97·3; 1 : 4-methylcyclohexanol, 96; propyl alcohol, 102·4; isopropyl alcohol, 105. With *m*-nitrobenzoyl chloride: quinol, 100; resorcinol, 107; catechol, 84·2; benzyl alcohol, 100. T. H. P.

Rapid, Accurate Determination of Acetone. Application to Biological Liquids. R. Gros. (*J. Pharm. Chim.*, 1934, **126**, 214–220.)—The precipitation of acetone by Nessler's reagent (*cf.* Bougault and Gros, ANALYST, 1922, **47**, 405) may be used for the accurate determination of acetone. The reagent is prepared in two parts: (A) 13·55 grms. of mercuric chloride and 36 grms. of potassium iodide are dissolved in water to 250 ml. (B) 540 grms. of sodium hydroxide are dissolved in water to 1 litre; 2 volumes of (A) and 1 volume of (B) are mixed immediately before use. The acetone is distilled off under a vacuum from a 250-ml. Erlenmeyer flask heated on a boiling water-bath, and is absorbed in the reagent contained in a special absorption pipette. The distillation occupies about 15 minutes, after which the flask is cooled and then again heated for 15 minutes and cooled. The vacuum is then released and the precipitate formed is washed several times (until free from chloride), either in the bulb of the pipette or in a centrifuge tube, the wash-water being poured through a weighed filter-crucible (1G4 or 2G4), in which the precipitate is ultimately collected and washed, under suction, with alcohol and

then with ether. The weight of the precipitate, dried at 100° C. to constant weight, is multiplied by 0·0325 to obtain the weight of acetone.

To determine acetone in urine, 5 ml. of the urine are mixed in a 50-ml. flask with 1 ml. of basic lead acetate solution and about 20 ml. of water. After 1 to 2 minutes, 10 drops of dilute sulphuric acid (1 : 10) are added, and the solution is made up to 50 ml. with water, mixed and filtered. Alkaline urines should be neutralised with hydrochloric acid prior to the defecation. Of the clear filtrate, 5 ml. are used, as described above, for the determination of the acetone. When blood is to be tested, defecation is effected by treatment with an equal volume of 20 per cent. trichloroacetic acid solution. Check determinations have given satisfactory results. T. H. P.

Use of 2,4-Dinitro-phenylhydrazine as a Quantitative Reagent for Carbonyl Compounds. I. Benzaldehyde. R. E. Houghton. (*Amer. J. Pharm.*, 1934, **106**, 62–64.)—A rapid, simple, economical and accurate method for the determination of benzaldehyde is proposed by means of 2,4-dinitrophenylhydrazine. The benzaldehyde (0·1 grm.) is dissolved in 5 ml. of ethyl alcohol, diluted with 50 ml. of water, and to this is slowly added, with constant stirring, a reagent prepared by dissolving 0·25 grm. of 2,4-dinitrophenylhydrazine in 2·5 ml. of concentrated sulphuric acid and adding 50 ml. of water. The precipitate is stirred until it settles, and, after standing overnight, is filtered off on a tared Gooch crucible, washed with about 15 ml. of 2 *N* sulphuric acid, and then with water, until this gives no precipitate with barium chloride, and subsequently dried at 110° C. to constant weight. The stirring and digestion of the precipitate overnight are necessary to reduce occlusion of the reagent and to facilitate filtration. A series of ten duplicate determinations showed individual differences between 0·01 and 0·66 per cent. D. G. H.

Anti-oxygens of Fatty Oils. Action of *p*-Nitraniline. M. Nakamura. (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 86B.)—The oxidation of oils with iodine values above 120 is accelerated by *p*-nitraniline to an extent nearly proportional to the iodine value. On oils with iodine values below 120, *p*-nitraniline begins to exert an anti-oxygen effect; this phenomenon of inversion takes place the more quickly, the lower the iodine values. Inversion of catalysis is correlated entirely with the iodine value, and not with any minor ingredient of the oil. R. F. I.

Oleic-Elaidic Acid Transformation as an Aid in the Analysis of Mixtures of Oleic, Linolic and Linolenic Acids. H. N. Griffiths and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1934, **53**, 75–81T.)—The quantitative conversion of higher monoethylenic *cis*-acids into their *trans*-(elaidic) forms, by means of the mercury and nitric acid reagent of Poutet in the proportions recommended by Archbutt (*J. Soc. Chem. Ind.*, 1886, **5**, 303), results in the production, at equilibrium point, of a product containing elaidic acid corresponding with 66 per cent. of the oleic acid originally present. This process has been applied to mixtures of acids. The procedure for the determination of oleic acid (as elaidic acid) in a mixture of fatty acids is to saponify the fresh oil, to recover the mixed fatty acids with minimum exposure to air, and to distil them as rapidly and as

completely as possible at a pressure of 1 mm. or less, so as to obtain representative samples. The distilled acids (10 to 20 grms.) are shaken with mercury (0·2 to 0·4 grm.) and nitric acid (0·5 to 1 ml.) of sp.gr. 1·4 in a stoppered vessel immersed in water at room temperature for 1 hour, and, after standing overnight, the product is extracted with ether, and the solution is washed with dilute nitric acid and then with hot water. Water and ether are removed, the product is boiled with about 100 ml. of petroleum spirit, and the clear solution is decanted from the resinous material, which is washed two or three times with 20-ml. portions of petroleum spirit, the washings being added to the main solution. The solvent is removed, and the acids are submitted to the petroleum spirit and lead salt process. The solid acids obtained from the insoluble lead salts are again treated with petroleum spirit and re-submitted to the usual lead-salt procedure. From the yield and iodine value of the solid acids the quantity of elaidic acid is obtained, and therefrom the maximum percentage of oleic acid in the original mixed acids. The method was applied to the acids of olive, cotton-seed, tea-seed and ground-nut oils, in which oleic and linolic are the only unsaturated acids, and the proportions of oleic acid found were in each case in fairly close agreement with those obtained by the ester fractionation method. When oleic, linolic and linolenic acids were all present, as in linseed, hemp-seed, rubber-seed, walnut, soya-bean, and wallflower-seed oils, determinations were also made by the bromination and thiocyanogen methods (for which details of procedure are given). Values obtained by the elaidic process were in every case very close to those derived from the thiocyanometric analyses, but both were quite different from the corresponding figures deduced from the amounts of insoluble hexabromostearic acid isolated. The agreement was found to be so consistent that the elaidic method, when applied to the quantitative analysis of highly unsaturated oils, is regarded as an independent confirmation of the utility of the thiocyanometric method, but it is more intricate and tedious than the latter method. Due precautions are needed with these unsaturated oils to ensure complete attainment of normal equilibrium, and correct separation of the elaidic acid, and the particular behaviour of the individual unsaturated oils is given in detail (*cf.* ANALYST, 1934, 312). D. G. H.

Gelation of China Wood Oils (*Aleurites*) by Antimony Halides. T. François. (*Compt. rend.*, 1934, **198**, 1046–1048.)—If, drop by drop, the oil of *Aleurites Fordii* or of *Aleurites montana* is poured into a chloroform solution of antimony chloride, each drop immediately becomes a gel, but the oils of *Aleurites moluccana* and of linseed remain liquid; this reaction may be used for the identification of the oils and the detection of adulteration. Two ml. of a 10 per cent. solution of antimony trichloride in chloroform are placed in each of a series of test-tubes (12 × 14 × 160 mm.), and four drops of the sample of oil are added from a dropper, with constant stirring. With pure tung and montana oils, the mixture is coloured a caramel-brown, and total gelation is immediate. If 20 per cent. of foreign oil is present, gelation takes 1 or 2 minutes; if 40 per cent., 10 to 15 minutes, and the product is sticky, adhering to the sides of the tube. The degree of purity of an oil may rapidly be found with a minimum precision of 10 per cent. by making known additions of arachis oil, for example, and the amount of tung oil in a linseed

oil may be found by determining how much of an authentic tung oil is needed to bring about gelation. Oils thickened by heating to the flash-point and rapidly cooled behave like the original oils from which they were derived. When studying the behaviour of mixtures of such thickened linseed and tung oils, 6 drops should be taken; gelation of the thickened tung oil takes 1 minute. D. G. H.

Inorganic Analysis

Nitrazine Yellow, a New Indicator. H. Wenker. (*Ind. Eng. Chem.*, 1934, **26**, 350.)—Nitrazine yellow is 2,4-dinitrobenzene-azo-1-naphthol-3,6-disulphonic acid; in acid aqueous solution the colour is bright yellow, whilst the alkaline solution is deep blue. The colour-change takes place between p_H 6·4 and 6·8, with a sharp neutral point at 6·6. W. P. S.

2,3-Diaminophenazine as a Reagent for Metal Ions. T. Pavolini. (*Ind. Chimica*, 1933, **8**, 692–694; *Ann. Chim. anal.*, 1934, **16**, 123.)—A solution of 2,3-diaminophenazine gives a red precipitate with cupric and mercuric ions, which may be tested for as follows:—To the solution, neutralised to litmus, are added 10 to 20 drops of an alcoholic solution of 2,3-diaminophenazine hydrochloride (0·5 per cent.), the liquid is well shaken, and any red colour in the foam produced is observed. The sensitiveness is $1 : 1 \times 10^5$ for mercury, and $1 : 6 \times 10^6$ for copper. The compound may also be used as a drop reagent. Ammonium salts interfere when in concentration greater than 2 to 3 per cent. Iron interferes owing to the masking of the red colour by precipitated basic compounds. Bismuth, lead and cadmium yield yellow or orange-coloured precipitates, but these reactions are of low sensitiveness. S. G. C.

Analysis of Sodium Stannate Tin-plating Solutions. A. W. Hothersall, S. G. Clarke and D. J. Macnaughtan. (*J. Electrodepositors' Tech. Soc.*, 1934, **9**, 118–121.)—The successful operation of alkaline sodium stannate tin-plating baths depends on controlling the free sodium hydroxide-content within narrow limits, maintaining a substantial concentration of quadrivalent tin, and avoiding the formation of bivalent tin in the solution. *Sodium Hydroxide.*—This may be titrated with acid after the addition of an excess of barium chloride, which precipitates as barium salts the interfering stannate and carbonate. Five ml. of the tin-depositing solution are transferred to a conical flask of about 400 ml. capacity, and 50 ml. of barium chloride solution (10 per cent.), and 1 drop of thymolphthalein indicator solution (1 per cent. in ethyl alcohol) are added. The suspension is titrated with standard hydrochloric acid (0·1 *N*), with vigorous shaking, until the blue colour produced by the thymolphthalein begins to be discharged. A further 1 drop of indicator is then added, and the titration is continued. The end-point is taken when the colour changes from a definite blue to practically white; this occurs comparatively sharply over a range of a few tenths of 1 ml. of titrating acid. One ml. of 0·1 *N* hydrochloric acid = 0·004 grm. of sodium hydroxide. *Colorimetric Method for Quadrivalent Tin.*—A rapid approximately quantitative method has been devised, suitable for works control, based on the production of a yellow turbidity of stannic iodide in 1 : 2 sulphuric acid,

which can be compared colorimetrically. The method is applicable to amounts of tin from 0·0001 to 0·001 grm. A 0·1-ml. sample of the tin-depositing solution (containing about 10 to 100 grms. of tin per litre) is taken by means of a capillary-bore pipette, and diluted to 10 ml. with 1 : 2 sulphuric acid (a mixture, cooled to room temperature, of 1 vol. of concentrated sulphuric acid with 2 vols. of water). Into each of two test-tubes of the same dimensions (approximately 20 ml. capacity), marked "1" and "2," and each provided with a glass stirring-rod, are placed 0·5 ml. of potassium iodide solution (20 per cent.) and 9 ml. of cold 1 : 2 sulphuric acid, and the solutions are well mixed. Into tube 1 is run 1 ml. of the diluted sample, and the whole is mixed by stirring. Without delay, standard stannic sulphate solution (see below) is run from a small burette into tube 2, in small quantities at a time, with stirring, until a yellow turbidity similar in degree to that present in tube 1, is produced. The comparison is best made by holding the tubes close together in the hand, and observing them at a distance of some 15 inches or more from the eyes; it further aids in a satisfactory comparison if the relative position of the tubes is reversed a few times during the observation; before the final comparison is made, the volumes should be made the same by the addition of 1 : 2 sulphuric acid. When the turbidities match, the amount of tin added to tube 2 is equal to that present in tube 1. The standard stannic sulphate solution is prepared by dissolving 1 grm. of metallic tin in 50 ml. of concentrated sulphuric acid by heating, boiling for a few minutes to ensure the oxidation of the tin, cooling, diluting with two parts by volume of water, again cooling, and, finally, diluting to 1 litre with 1 : 2 sulphuric acid (1 ml. $\equiv$ 0·001 grm. of tin). It is noted that (*a*) the comparison should be carried out as rapidly as possible, as the turbidity gradually changes in appearance, owing to the growth of particles, etc., and iodine is slowly liberated; (*b*) both stannic and stannous sulphates give similar yellow turbidities; (*c*) the turbidity is prevented from forming in the presence of chloride, partially or completely according to the amount present; (*d*) the turbidity decreases to nil as the sulphuric acid concentration is reduced. *Other Methods.*—Other methods include the accurate determination of quadrivalent tin by reduction with hypophosphorous acid and subsequent titration with iodine (Evans, ANALYST, 1931, **56**, 171), determination of bivalent tin by titration with iodine, and determination of carbonate by Hepburn's method (ANALYST, 1926, **51**, 662).

S. G. C.

New Reaction of Triethanolamine with Cobalt Salts. F. Garelli and T. Tettamanzi. (*Ind. Chimica*, 1933, **8**, 577–578; *Ann. Chim. anal.*, 1934, **16**, 129.)—The addition of a few drops of cobalt chloride solution (5 per cent.) and a little ammonia to an aqueous solution of triethanolamine yields a violet-red colour with as little as 0·5 part of triethanolamine per 100,000. Conversely, triethanolamine may be used to detect cobalt; small amounts of nickel do not interfere.

S. G. C.

Interference of Nitric Acid in the Permanganate Titration of Iron. D. Totoiescu. (*Z. anal. Chem.*, 1934, **96**, 183–188.)—The author observed that the presence of nitric acid in the permanganate titration of iron, when reduction zinc and sulphuric acid has been used, leads to high results; the nitric acid is

reduced to a large extent to hydroxylamine, which consumes permanganate. Hence, if nitric acid has been introduced, it should be entirely removed by evaporation with sulphuric acid practically to dryness. If necessary, the evaporation should be repeated. The titrated liquid should give a negative reaction with diphenylamine. W. R. S.

Detection of Small Quantitities of Tantalum and Niobium. W. R. Schoeller. (*Z. anal. Chem.*, 1934, **96**, 252–257.)—The precipitation of the coloured tannin complexes is recommended for the identification of tantalum and niobium in small quantities of minerals; the reaction is shown to be more sensitive, specific, and convenient than those proposed by Rienäcker and Schiff, *i.e.* hydrolytic precipitation of tantalic acid, and formation of a lake of niobium sesquioxide with alizarin (*Z. anal. Chem.*, 1933, **94**, 415). About 2 mgrms. of powdered mineral are fused in a small silica crucible with a speck of potassium bisulphate, and the melt is dissolved in 1 to 2 ml. of ammonium oxalate solution. The solution is treated at the boiling-point with about 0·1 grm. of ammonium chloride and 0·02 grm. of tannin (solid), and left for a short time. The yellow tantalum precipitate permits of the detection of 0·05 mgrm. of Ta_2O_5 per ml.; the niobium reaction (red precipitate) is approximately three times as sensitive. Iron does not interfere in the slightly acid oxalate solution. If the mineral contains titania (hydrogen peroxide test) it is fused with bisulphate, and the melt is extracted with 5 per cent. sulphuric acid containing one per cent. of tannin (ANALYST, 1929, **54**, 453); the coloured residue containing the earth acids may be tested, after ignition, by the above reaction. W. R. S.

Colorimetric Determination of Uranium in Low-Grade Ores. J. Tschernichow and E. Guldina. (*Z. anal. Chem.*, 1934, **96**, 257–263.)—The procedure is based on the coloration of uranyl ferrocyanide; the elimination of iron is effected by electrolysis with the mercury cathode. The ore (0·5 grm.) is gently boiled with 20 ml. of sulphuric acid (1 : 4) and 5 ml. of hydrochloric acid for 30 minutes. The filtered solution is precipitated with 5 ml. of 3 per cent. hydrogen peroxide and carbon dioxide-free ammonia. The washed precipitate is dissolved in very little hot 1 per cent. sulphuric acid, and the solution (maximum volume 50 ml.) is electrolysed with a mercury cathode at 4 to 5 amperes and 6 to 8 volts until the iron reaction with ferricyanide on a spot plate becomes negative. The electrolyte is precipitated with ammonia as before, the precipitate being washed and dissolved in 3 per cent. sulphuric acid. The solution is treated with ammonia until faintly cloudy, and cleared with a few drops of *N* sulphuric acid. The uranium is precipitated free from vanadium by 5 ml. of 6 *N* acetic acid and 15 ml. of *M*/3 disodium phosphate. If the amount of alumina present is small, a little alum solution (5 mgrms. of Al_2O_3) should be added. The solution is boiled, and filtered after 10 minutes, and the precipitate is washed 5 to 6 times with *N* ammonium nitrate solution. The phosphate precipitate is dissolved in hot 0·2 per cent. sulphuric acid, with which the solution is made up to 100 ml. Ten ml. of the solution are treated in a glass cylinder with 5 ml. of a 10 per cent. solution of potassium ferrocyanide containing 1 per cent. of sodium sulphite, and, after a few minutes, the tint is matched against those of a series of standard tubes containing

1, 2, 3, ... 7 ml. of a solution of uranium sulphate free from iron. This solution is prepared from one of uranyl nitrate of known strength by precipitation with ammonia, solution of the precipitate in 0·2 per cent. sulphuric acid, and adjustment of the concentration to 0·1 mgrm. of U_3O_8 per ml. by means of the same acid. A closer result is obtained by a second match of freshly-prepared unknown solution against a fresh scale of 3 tubes, the strongest and weakest of which correspond to the two neighbouring tubes of the first scale between which the unknown has been located, while the intermediate tube contains 0·5 ml. of standard uranium solution less than the stronger of the two. Residues and by-products containing organic matter must be ignited prior to the determination. W. R. S.

Microchemical

Micro-Iodimetric Determination of Iron. J. Straub. (*Mikrochem.*, 1934, **14**, 251–255.)—Neumann's method (*Z. physiol. Chem.*, 1902–3, **37**, 115; 1904–5, **43**, 32) is found to give incorrect results for amounts of iron less than 0·05 mgrm. For amounts of iron from 0·5 to 0·01 mgrm. good results are obtained when 2 to 3 drops of concentrated hydrochloric acid are added to 8 to 9 ml. of the test solution and 1 to 2 grms. of potassium iodide, and the liberated iodine is titrated against *N*/500 sodium thiosulphate solution, with starch as indicator. Organic matter may be destroyed by ashing the material in a platinum crucible, treating the residue with 2 to 3 drops of hydrochloric acid, and adding 2 to 3 drops of perhydrol. After this mixture has been evaporated to complete dryness the residue is taken up in 2 to 3 drops of hydrochloric acid and transferred to the conical flask by means of 8 to 9 ml. of water, and the determination is carried out as before. Alternatively, the organic matter may be decomposed by adding fuming nitric acid and heating until a white residue is obtained; this is taken up in hydrochloric acid and the iron is determined as before. J. W. B.

Quantitative Micro-analysis of Uranites. F. Hecht and W. Reich-Rohrwig. (*Mikrochem.*, 1933, **12**, 281–292.)—A scheme for the complete micro-analysis of uranite minerals is described for an initial weight of about 35 mgrms. The mineral is dissolved in nitric acid (1 : 1), and filtered from the insoluble matter, which is ignited and weighed, and the silica is volatilised with hydrofluoric acid in the presence of sulphuric acid. The soluble silica in the filtrate is rendered insoluble by repeated evaporation with nitric acid and determined. The nitrates are then converted into chlorides, and hydrogen sulphide is passed through the solution to precipitate metals of the sulphide group. On treatment with yellow ammonium sulphide a very small trace of substance dissolves which is tabulated as SnO_2(?). The residue of lead sulphide (bismuth is normally absent) is dissolved in nitric acid, the solution is evaporated with sulphuric acid, and the lead is weighed as lead sulphate. The hydrogen sulphide in the filtrate is destroyed by evaporation to dryness and oxidation with a little nitric acid, and then iron, aluminium, thorium and the rare earths (including titanium and zirconium) are precipitated with ammonia in the presence of 0·6 to 0·7 grm. of hydroxylamine

hydrochloride, and are thus separated from uranium, calcium and magnesium; this precipitation is repeated once or twice. In the combined filtrates the hydroxylamine and most of the ammonium salts are destroyed by evaporation with nitric acid. The precipitation with hydroxylamine is again repeated, the reagent is destroyed as before in the filtrate, and then uranium is precipitated as oxime in acetic acid solution, and finally weighed. The filtrate is evaporated, the residue is ignited, calcium is determined by precipitation with picrolonic acid, and finally magnesium is precipitated with sodium phosphate in the filtrate from the calcium, ignited to pyrophosphate and weighed as such, or converted into the oxime by precipitation with 8-hydroxyquinoline in alcoholic ammoniacal solution (Strebinger and Reif, *Mikrochem., Pregl-Festschrift*, 1929, 319). The hydroxide precipitate of iron, aluminium, chromium and the rare earths is dissolved in nitric acid. Thorium and part of the rare earths are precipitated with malic acid, and filtered off, and the filtrate is treated with ammonia until the reaction is only weakly acid; the new precipitate of rare earths is filtered off, and both fractions are separately ignited and weighed as oxide. In the filtrate, after destruction of the oxalic acid, iron and aluminium are precipitated with ammonia and ignited and weighed as oxides. The oxides of thorium and the rare earths are brought into solution by treatment with pyrosulphate and then nitric acid, the first fraction is precipitated with ammonia and filtered off, the precipitate is dissolved in nitric acid, and in the combined solution of the nitrates of both fractions the thorium is separated from the rare earths, after removal of the acid, by conversion into the hydrated peroxide, by means of ammonium nitrate and hydrogen peroxide. The separation is repeated, and finally the precipitate is ignited and weighed as thorium dioxide.

The total sulphur is determined in a separate portion of the mineral, which is fused with ten times the amount of a mixture of sodium carbonate and sodium nitrate (3 : 2) in a porcelain crucible in an electric furnace. The melt is treated with water and filtered, and the residue is washed, first with water and then with 1 per cent. sodium hydroxide solution. Finally, the filtrate and washings are cautiously acidified with gaseous hydrogen chloride. The silica is separated by evaporation with hydrochloric acid, the uranium and aluminium in the filtrate are precipitated with ammonia (free from carbon dioxide), the liquid is filtered, the filtrate is acidified with hydrochloric acid, and the sulphate is determined as barium sulphate. The *apparatus* used comprised the following: Berlin porcelain crucibles of outside top diameter 33 mm., bottom diameter 19 mm., a height of 43 mm. and a capacity of 25 cm.; Emich filter-sticks, with porcelain filtering surface (Berlin Porzellan Fabrik); platinum crucibles, with a top diameter of 28 mm., bottom diameter 17 mm., height 40 mm., and capacity 20 ml.; platinum Neubauer filter-sticks (from Heraeus, Hanau); electrically-heated water-bath (author's design), with suction to aid evaporation (from P. Haack, Vienna). For gas-inlet a special cover-glass, with an inlet-tube passing through it, was used to avoid contamination. When the precipitates were to be weighed without ignition, filter-beakers were used (*Recent Advances in Analytical Chemistry*, Vol II, *Micro-Analysis*). A glass stand was used for the dropping pipettes, by means of which the liquid reagents were added. A number of analyses, in which the sum of the results ranges from 98·33 to 100·42 per cent., are cited. J. W. B.

"Spot" Tests for Hydrogen Peroxide. F. Feigl and E. Fränkel. (*Mikrochem.*, 1933, **12**, 303–306.)—(i) *By formation of Prussian blue.*—A drop of the dilute solution under examination is mixed on a spot-plate with a drop of reagent (equal volumes of 0·4 per cent. ferric chloride and 0·8 per cent. potassium ferricyanide solution). An intense blue colour or precipitate indicates hydrogen peroxide. A blank must be carried out. The same reaction occurs with other reducing substances, such as stannous chloride, thiosulphate, nitrites, and sulphites. *Smallest amount detectable*: 0·08 γ of H_2O_2; *Limit of dilution*: 1:600,000.

(ii) *By decolorisation of the higher oxide of nickel.*—Hydrogen peroxide is catalytically destroyed by nickel hydroxide, and from higher oxides of nickel the divalent oxide or hydrated oxide is formed. The test depends on the disappearance of the black colour of the nickel hydroxide, which is used in admixture with barium sulphate in the form of a paste. A blank must be carried out. *Smallest amount detectable*: 0·01 γ of H_2O_2. *Limit of dilution*: 1:5,000,000. To make the paste, baryta water is mixed with bromine water, and the resulting barium hypobromite is mixed with nickel sulphate and warmed. The proportions should be such that a grey precipitate is formed. This is filtered off and washed and can be kept for a long time in a moist condition in a stoppered bottle.

(iii) *By formation of peroxo-vanadates.*—The test may be used either for the detection of peroxides or vanadates: The yellow peroxo-vanadate, $\left(V\langle{}^{O}_{O}\rangle\right)_2(SO_4)_3$, in converted into yellow ortho-peroxo-vanadic acid according to the equation: $(VO_2)_2(SO_4)_3 + 6H_2O \underset{H_2SO_4}{\overset{H_2O_2}{\rightleftharpoons}} 2(VO_2)(OH)_3 + 3H_2SO_4$. Thick filter paper ("spot" paper) is impregnated with a 1 per cent. alkali vanadate solution, slightly acidified, and dried. On adding a drop of peroxide solution, a yellow to rose-red fleck is formed. *Smallest amount detectable*: 3 γ of H_2O_2. *Limit of dilution*: 1:16,600.

(iv) *By reduction of gold salts.*—$2\,Au\,Cl_3 + 3H_2O_2 = 6HCl + 2\,Au + 3O_2$. A drop of a 0·01 per cent. gold chloride solution is warmed in a micro-crucible with a drop of the hydrogen peroxide solution. A red or blue colour, due to colloidal gold, indicates the presence of a peroxide. *Smallest amount detectable*: 0·07 γ of H_2O_2. *Limit of dilution*: 1:714,000.

(v) *With alkali thiocyanate.*—About 1 ml. of a 5 per cent. solution of an alkali thiocyanate is acidified with sulphuric acid and warmed with a drop of the peroxide solution; according to the amount of peroxide present, a red-yellow precipitate or colour appears. *Smallest amount detectable*: 0·7 γ of H_2O_2. *Limit of dilution*: 1:71,000. J. W. B.

Micro-Determination of Phosphorus as Phosphomolybdate. R. H. A. Plimmer. (*Biochem. J.*, 1933, **27**, 1810–1813.)—The determination of phosphorus in organic matter by the volumetric determination of ammonium phosphomolybdate (a method in use since 1906) is accurate for quantities of phosphorus ranging from 1 to 30 mgrms. From 1914 to 1933 various workers have maintained either that the method is inaccurate for micro-quantities, or of no value for quantities below 0·1 mgrm. Greenwald (*J. Biol. Chem.*, 1913, **14**, 369) and Taylor and Miller (*J. Biol. Chem.*, 1914, **18**, 215), however, obtained satisfactory results

with quantities of 0·015 to 0·12 mgrm. Pregl (*Quantitative Organische Mikroanalyse*), who weighed the precipitate, regarded the process as accurate, and quotes Lieb as proving the method applicable volumetrically to 0·03 mgrm. It is generally agreed that excellent results are given with quantities ranging from 0·1 to 10 mgrms., and the author has carried out an investigation to ascertain the reason for the general failure with the micro-quantities. He shows that the accurate determination of micro-quantities of 0·01 to 0·1 mgrm. of phosphorus by the molybdate method depends upon: (1) the conditions of precipitation; 20 ml. of 10 per cent. ammonium nitrate solution must be present for every ml. of concentrated sulphuric acid; (ii) the use of a purified solution of ammonium molybdate, such as that of Pregl; and (iii) the filtration of the precipitate on an asbestos filter such as that of Bertrand. For quantities above 1 mgrm. of phosphorus the perforated platinum plate is preferable. With the procedure described, four determinations can be made in 1 hour. The sensitivity of the precipitation of ammonium phosphomolybdate under the described conditions has been tested qualitatively. Quantities of phosphorus from 0·009 to 0·006 mgrm. in about 25 ml. began to come down in 2 to 3 minutes; from 0·005 to 0·003 mgrm. in 6 to 12 minutes; 0·002 mgrm. showed on standing 1 hour, and 0·001 mgrm., which was just visible but quite evident on filtering on to the asbestos, in 1½ hour. The micro-method is applicable to solutions of inorganic phosphate and to all forms of organic phosphorus for determination of total phosphorus. Inorganic phosphate in the presence of phosphoric esters not rapidly hydrolysed by acid, such as are present in blood-filtrates, can be determined, especially if filtration is carried out after 15 minutes, or if the precipitation is allowed to proceed at room temperature overnight. P. H. P.

Physical Methods, Apparatus, Etc.

Nickel Salts as Light Filters. W. V. Bhagwat. (*J. Indian Chem. Soc.*, **1934, 11**, 5–11.)—The limits for the transmission of light by nickel sulphate solutions are as follows:

Concentration	Range of transmission $m\mu$	Max. transmission Per Cent.
5·28 *N*	440–620	53·7
2·3 *N*	400–680	79·4
0·9 *N*	All	89·1

Nickel salts, when used in combination with cobalt salts, transmit solely in the ultra-violet region, and, therefore, form suitable light filters for ultra-violet photography.

Salt	Time of exposure Hours	Transmission: Visible $m\mu$	Transmission: Ultra-violet $m\mu$
(i) 2·08 *M* nickel sulphate + 1·83 *M* cobalt chloride; each in 1 cm. quarter cell	4	560–630	330·7–359·8
(ii) 4·16 *M* nickel nitrate + 3·66 *M* cobalt chloride	4	Nil	342·0–352·7 (faint)
(iii) 2·08 *M* nickel nitrate + 3·66 *M* cobalt chloride	4	Nil	330·7–359·8
(iv) 3·66 *M* cobalt chloride	4	710–760	261·4–406·3

Reviews

AN INTRODUCTION TO BIOCHEMISTRY. By Prof. W. R. FEARON, M.A., Sc.D., M.B., F.I.C. Pp. x + 313. London: William Heinemann (Medical Books), Ltd. 1934. Price 10s. 6d. net.

Perhaps the most startling thing about this book is the opening sentence of the Preface, which reads "I have sought to approach the living organism, and to lead such as may be disposed to follow me, along the less worn path of *inorganic biochemistry*." Professor Fearon, whose volume is dedicated to Sir Frederick Hopkins, and therefore raises in the reader expectations of a very high standard, has been compelled by the unfairness of nature, which insists upon being much more organic than inorganic, to depart from the more startling implications of his introductory fanfare.

Chapters I, II and III, on The Subject Matter of Biochemistry, The Biological Elements, and Inorganic Compounds, respectively, give place to a series of chapters on the various well-recognised groups of organic substances, right up to Chapter XIX on Autacoids, a somewhat unusual term coined by Schaefer to replace "internal secretion" or "hormones."

It can be said at once that the book is packed with information, well arranged and set up, and substantially free from serious errors of fact or typography. It is clearly written, with the advanced student primarily in mind, but this will not prevent its being one of the best summaries of modern biochemistry for the use of analytical and other practising chemists.

Other reviewers have already commented on the fact that this book, published early in 1934, has succeeded in bringing the story of biochemistry almost up to the end of 1933. In the course of this achievement, however, a few slips have clearly proved unavoidable. For example, the careful student is likely to be puzzled by the consecutive attribution to ergosterol of the formulae $C_{27}H_{41}OH$ (p. 129), and $C_{28}H_{44}O$ (p. 130); the latter is, of course, in accordance with modern views. Also Dr. Fearon seems to be a little at sea about the correct use of the symbol "λ"; he appears to think it interchangeable with $m\mu$.

The up-to-date and complete scope of this book is exemplified by the inclusion of references to several important recent pieces of work, such as that on the common chrysene nucleus of many substances of physiological action, the synthesis of certain carcinogens (though no mention has been found of the fact that some are also oestrogenic), the identification of vitamin *C* with ascorbic acid (though not its synthesis).

In the excellent chapter on Food and Vitamins no space is given to one very important pharmacological principle, namely, the use of international standard preparations as unit substances, to avoid the difficulties that arise in assays when an attempt is made to use some "unit" of animal reaction. There is a great deal of confusion still on this point, and a failure to distinguish between the existence of an international unit and an international standard preparation; the sooner students are made to understand the position clearly, the better for everybody.

If, as is to be hoped, Professor Fearon finds himself soon called upon for a new edition of this book, he would be well advised to include therein some reference to the increasing use of spectroscopic methods in biochemical work; a reference to the recent introduction of the so-called chromatographic analysis might also not be out of place.

A. L. BACHARACH

FUNDAMENTALS OF BIOCHEMISTRY. T. R. PARSONS, B.Sc., M.A. Fourth Edition. Pp. xii + 436. Cambridge: W. Heffer & Sons, Ltd. 1933. Price 10s. 6d. net.

The author's aim in this edition, as in the first edition of 1922, has been to give students new to the subject an introductory account of the more important biochemical aspects of human physiology. It may be said at once that the book represents a real accomplishment, for, with only an elementary knowledge of organic chemistry, a student will be able to follow the author readily throughout the course he has set, and not less because of his very readable style. Perhaps in the desire to make his book an entrancing "story rather than a catalogue," the author has been led into some curiosities of expression not usually found in a scientific text-book, as on p. 125, for example, where he refers to saponification thus: " . . . if we take an ester and stew it up with caustic soda . . . " But this is by the way.

To others besides the student, this book will be found interesting and refreshing. To the chemist generally, and particularly to one who is interested in the constituents of foodstuffs and their fate in the body, it is a stimulating treatise, though small, and modest in its aim. It gives a clear and concise account of our newer knowledge on the constitution of the proteins, and on vitamins, enzymes, and body-pigments.

In the Chapter on "Fats and their Metabolism," the interesting statement is made (p. 131) that "a foreign fat fed to a lactating animal may appear in its milk." Put baldly in this way, it might be taken to involve serious difficulties to the analyst in the examination of milk and milk products, but few would be found to affirm that there is in practice any real difficulty due to such a cause. On p. 337, the strength of a sodium chloride solution isotonic with mammalian blood is given as 0·95 per cent., instead of the usual 0·85 per cent.

In the Chapter (XII) on "The Human Machine," the author gives in some 40 pages a thoroughly adequate summary of our knowledge of the fuel requirements and energy output of the human body that can be recommended to all interested in this fascinating subject.

The book as a whole has impressed the reviewer with its value both to the student and to the food chemist. Each chapter is succeeded by a short summary and bibliography, and there is a good index. The type and general make-up of the volume are excellent.

ARNOLD R. TANKARD

QUALITATIVE CHEMICAL ANALYSIS. By ROY K. MCALPINE, Ph.D., and BYRON A. SOULE, Sc.D., University of Michigan. Based upon the text of A. B. Prescott and O. C. Johnson. Pp. xii+697. London: Chapman & Hall, Ltd. 1933. Price 21s. net.

The sub-title of this book states that it gives "Certain Principles and Methods used in identifying Inorganic Substances, together with a systematic Survey of the Chemistry of these Materials." Like some other transatlantic books on the subject, it is written expressly (sometimes a little too obviously) for college tuition—as shown in passages such as the following: "in order that a fair range of ground may be covered in a single semester it is necessary that the scheme of analysis be fairly simple" (p. 6).

The text-matter comprises 145 pages of theoretical considerations, 285 closely-printed pages on the chemistry and reactions of metals, 138 pages on the non-metals, and 38 pages on the systematic examination of unknown substances. The copious appendix includes a chapter on the balancing of equations. Numerous footnotes on almost every page refer to the most recent original literature. The analytical and general chemistry of the commoner elements is treated with a wealth of detail which raises a doubt as to whether this type of book is suitable as an introduction to analytical chemistry. The student is advised "to browse through" this massive tome; but, considering the short time put at his disposal in the curriculum, one may perhaps be allowed to wonder whether the average freshman can do more than nibble at this heavy fare without serious risk of mental indigestion. Rightly or wrongly, I believe that the learner should be introduced to the subject through more concise and elementary manuals, as generally used in British and Continental training institutions. Such preliminary survey of the whole field will enable those who desire to specialise in chemistry readily to take up a more advanced and detailed study of their principal subject.

As regards the common elements, the book is a reliable compilation of a multitude of facts and observations, and as such will be useful to inorganic and to analytical chemists. A few disputable statements were noticed, *e.g.* that cobalt "may be weighed as the cobaltinitrite" (p. 337), and that precipitated nickelic oxide has the formula $NiO_2.nH_2O$ (p. 343). The rarer elements are treated more succinctly, and the information is not always accurate. Two instances may be given. The table of the reactions of the platinum metals (p. 281) reproduces that in Newton Friend's Textbook (Vol. IX, 1920) with the inaccuracies I pointed out in the following passage when reviewing that work: "the yellow precipitate of potassium chloroplatinate has not been included; the yellow precipitate produced by dimethylglyoxime is attributed to ruthenium instead of palladium, whilst palladous chloride is wrongly stated to give a red precipitate of K_2PdCl_4. As a matter of fact, the chloropalladite, K_2PdCl_4, is readily soluble in water, whilst the red chloropalladate, K_2PdCl_6, is not."

The above is a case of uncritical reproduction of inaccurate statements. In the next instance the authors have committed a serious error in quoting from the original literature. In a brief mention of Powell and Schoeller's tannin process for the separation of tantalum from niobium, they make the following statement: "The tantalum precipitate is light brown in color; if contaminated with Cb it

is red" (p. 377). It seems hardly possible that anybody could have read the directions and yet missed the vitally important point, emphasised throughout the paper, that the pure tantalum precipitate is sulphur-yellow. Contamination with niobium produces an orange-coloured precipitate; a brown tantalum precipitate is produced only in presence of titanium or tungsten. W. R. SCHOELLER

NACHWEIS DER BIOLOGISCH WICHTIGEN KÖRPER DURCH FLUORESZENZ UND FLUORESZENZSPEKTREN. By CHARLES DHÉRÉ. Handbuch der biologischen Arbeitsmethoden. Edited by EMIL ABDERHALDEN. Section II, Physikalische Methoden, Part 3, No. 4. Pp. 3097 to 3306. Berlin and Vienna: Urban and Schwarzenberg. 1933. Price RM. 11.50.

"Abderhalden" has long joined the ranks of those publications which seem never to be completed, and its ramifications have led us into many unfamiliar backwaters of experimental biology. It is safe to speculate, however, that the present volume on the applications of fluorescence methods was not contemplated when the series was started several years back, since the development of the subject has been mainly during the last five years, and, indeed (apart from general matters of technique), a reference dated previous to 1928 is a rarity.

The book, which is well-illustrated, is divided into two almost equal portions, dealing with apparatus, technique and the physical chemistry of fluorescence phenomena, and with applications of the method, respectively. The first may, therefore, be read independently of any biological interests, and is an excellent account of the usual methods of generating ultra-violet light. Certain of the sources apparently available on the commercial scale in Germany, are of particular interest, and special mention may be made of the cadmium-vapour lamp. Vertical illuminators for microscopes which can be used with ultra-violet light are quite an innovation in fluorescence microscopy, and their inclusion is an indication of the general up-to-date standard of the book. Spectroscopical analysis of fluorescence is, of course, almost an essential feature of work connected with substances of biological interest, and here again descriptions and illustrations are given of the most recent apparatus. Strangely enough, the mercury-in-quartz lamp, which many workers have learned to regard as the most convenient source of ultra-violet light for fluorescence analysis, receives only scant attention, and one is left with the impression that this general opinion is, perhaps, not shared by the author.

The physico-chemical chapter is of distinct academic interest, but it is to the sections on the applications of the method that biological workers and analysts will turn with most interest. The former, at any rate, will not be disappointed, for they will find recorded masses of data, chiefly of a spectroscopical nature, and numerous observations which probably are more of importance as an aid to elucidating structures than as methods of actual detection. As might be expected, considerable attention is devoted to the proteins, and, in particular, to the fluorescence of porphyrin and chlorophyll, on which the author is probably the foremost authority, and certainly the most prolific worker.

Carbohydrates, fatty substances and alkaloids are also dealt with shortly, but the information throughout is rather of an academic character, and there is

little in it to assist the average analyst, whose equipment seldom consists of anything more elaborate than a mercury lamp, and who has no facilities for fluorescence spectroscopy. Thus, for example, insufficient stress is laid on the importance of standardised conditions, particularly of details, in carrying out work of this type, although (probably for this reason) the observations recorded with certain alkaloids are at variance with those obtained by other workers; the usefulness in this connection of capillary analysis might also have been emphasised.

At the same time, there is no claim that the volume is intended as a laboratory handbook for the general analyst, and it can certainly be unreservedly recommended to the specialist as the fullest account obtainable of the application of fluorescence methods to biological work.

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