THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Analytical Methods Committee

POISONS SUB-COMMITTEE

A SUB-COMMITTEE has been appointed to investigate methods of assay for various substances appearing in the Poison Schedules of the Poisons Rules, 1935. The Sub-Committee consists of Dr. G. Roche Lynch, O.B.E., M.B., B.S., D.P.H., F.I.C. (Chairman), Dr. C. H. Hampshire, M.B., B.S., B.Sc., F.I.C., Dr. W. H. Linnell, Ph.D., M.Sc., F.I.C., and Messrs. T. Tusting Cocking, F.I.C., C. E. Corfield, B.Sc., F.I.C., C. Edwards, B.Sc., F.I.C., N. Evers, B.Sc., F.I.C. (Hon. Sec.), B. F. Howard, F.I.C., W. A. N. Markwell, J. R. Nicholls, B.Sc., F.I.C., A. D. Powell, F.I.C., A. I. Robinson, and C. E. Sage, F.I.C.

The Sub-Committee is in the first instance considering preparations of lobelia, gelsemium, aconite and ephedra, and will be glad to receive from chemists (at home or abroad) details of any methods which have been found of service in the assay of these drugs, and will also welcome any suggestions relating thereto. Communications should be sent to the Hon. Sec. of the Sub-Committee, Mr. N. Evers, Messrs. Allen & Hanburys, Ltd., Bethnal Green, London, E.2.

Death

WITH great regret we record the death of Mr. W. Rintoul on August 25th.

Citric Acid in Milk and its Determination

By L. H. LAMPITT, D.Sc., F.I.C., and H. S. ROOKE, M.Sc., F.I.C.

Introduction.—Continuation of the work which was described some few years ago,[1] on the action of bacteria in milk, necessitated the determination of the various constituents attacked by micro-organisms, through a range extending from the amount in which they are normally found in milk to zero concentration. After some considerable experience of the method employed in the previous work for the determination of citric acid, it became evident that the method (a modified pentabromoacetone method) was not sufficiently accurate for all concentrations of the acid. As a result a study has been made of a large selection of the published methods for carrying out the determination in question. Two other points have also been considered: the actual separation of citric acid from milk, and the proof that the precipitate obtained from milk in the modified method of Kunz[2] is definitely pentabromoacetone.

PART I

The Isolation of Citric Acid from Milk Powder.

The presence of citric acid in milk was first reported by Soxhlet and Henkel[3] in 1888, but no confirmation of this finding was apparently forthcoming until 1918, when Sommer and Hart[4] isolated citric acid crystals from milk powder. Although the formation of a white precipitate from milk serum on addition of permanganate in presence of Denigès' reagent,[5] and of pentabromoacetone in the Kunz[2] method of determination, are strong presumptive proof that citric acid is present in milk, it was considered that the isolation of crystals of citric acid from milk powder, confirming the work of Sommer and Hart,[4] would be conclusive proof.

Table I

Analysis of the Crystals of Citric Acid obtained from Milk Citric Acid

	Citric acid from milk		Pure citric acid	
Equivalent of crystalline acid (titration with NaOH)	70·4	70·4	70·0	
Barium in anhydrous salt, per cent. ..	50·93	50·29	50·58	51·23
Calculated equivalent of anhydrous acid from per cent. of barium	66	68	67	65
Theoretical equivalent of anhydrous citric acid		64		

Method.—The method employed was that described by Sommer and Hart,[4]* except that the syrup containing the phosphoric and citric acids (after removal

* Casein precipitated with hydrochloric acid; serum neutralised to normal *p*H with sodium hydroxide and calcium hydroxide and precipitated albumin removed by filtration; serum concentrated to 1/10 volume and precipitate of calcium phosphate and citrate removed by filtration; precipitate dissolved in nitric acid; lead acetate added; lead precipitate decomposed with hydrogen sulphide; lead-free solution evaporated on water-bath to a syrupy solution.

of the lead) was extracted with dry ether, from which, after concentration and cooling, colourless crystals deposited. These crystals (after being recrystallised twice from water and dried in air) were characterised as citric acid by determination of the equivalent and by analysis of the barium salt (dried at 160° C.). The results obtained are given in Table I.

It is probable that the barium salts analysed were not completely anhydrous, but, as complete dehydration cannot be effected without noticeable decomposition occurring, no further drying was undertaken.

PART II

The Determination of Citric Acid in Milk.

(*a*) Summary of Methods.—The available methods for citric acid determination may be divided into the following groups:

(1) Pentabromoacetone methods; (2) mercurimetric methods (modifications of Denigès' method); (3) acetone methods; (4) miscellaneous methods.

The principles underlying the various processes are briefly as follows:

(1) *Pentabromoacetone methods.*—Citric acid is oxidised by means of potassium permanganate to acetone dicarboxylic acid, which is then caused to react with bromine to give pentabromoacetone.

(2) *Mercurimetric methods.*—Oxidation of citric acid in the presence of an acid solution of a mercury salt gives a complex basic double mercury salt of the acid with acetone dicarboxylic acid.

(3) *Acetone methods.*—On boiling a solution containing acetone dicarboxylic acid formed by oxidation of citric acid, carbon dioxide is lost and acetone produced, which may be determined either by Denigès' method or by Messinger's iodoform process.

(4) *Miscellaneous methods.*—The determination of carbon dioxide formed on oxidation of citric acid with permanganate in boiling solution is the basis of Weijer's[6] method, shown by Kuyper[7] to be uncertain. Pirrone[8] described an iodimetric method based on the oxidation of citric acid with potassium iodate. Other methods described include Thunberg's[9] citrico-dehydrogenase process using cucumber seed extract; the method is only suitable for very small quantities of citric acid and requires special technique. Pucher's[10] spectrophotometric method is based on the olive-green colour produced by the action of sodium sulphide on pentabromoacetone in petroleum spirit solution, and is intended for quantities of citric acid between 0·1 and 1 mg.

(*b*) Comments on Test Determinations employing Various Methods.—A selection of methods has been tested on pure citric acid and on citric acid in the presence of lactose. In each case the procedure described by the author was followed and the amount of citric acid calculated by use of the appropriate factors given in the original papers. Results obtained are given in Table II (*a* and *b*).

It is not proposed to comment in detail on the various methods tested. Certain of them are obviously not suitable for the determination of citric acid in milk unless the citric acid is first separated, *e.g.* as the barium salt. In the

TABLE II*a*

RESULTS OF TEST EXPERIMENTS

Method	Citric acid taken g.	Citric acid alone: Found g.	Citric acid alone: Average yield Per Cent.	Citric acid + 1·4 g. lactose: Found g.	Citric acid + 1·4 g. lactose: Average yield Per Cent.
Pentabromoacetone ..	See Table III.				
Mercury methods					
Beau[11] ..	0·0184	0·0101, 0·0126	61·7		
	0·0368	0·0351, 0·0355	95·9		
	0·0460	0·0444, 0·0435	95·7		
Gowing-Scopes[12]	0·0092	0·0077, 0·0079	84·7	Not applicable in the presence of lactose	
	0·0184	0·0153, 0·0154	83·4		
	0·0276	0·0234, 0·0229	83·9		
Rogina[13] ..	0·0092	0·0111	120·6	Results doubtful in the presence of lactose	
	0·0183	0·0208	113·7		
	0·0458	0·0502	109·6		
Acetone methods					
Kogan[14] ..	0·0183	0·0167, 0·0174	92·9	—	
	0·0458	0·0463			
		0·0480	103·3	—	
		0·0477			
	0·0916	0·0965, 0·0958	104·9	0·0965	105·3
Bartels[15] ..	0·0183	0·0167, 0·0175	92·9		
	0·0458	0·0464	101·3	0·0464, 0·0464	101·3
	0·0916	0·981, 0·0958	105·9	0·0957	104·5
Täufel and Mayr[16]	0·0183	0·0175, 0·0170	94·5	0·0190	103·9
	0·0458	0·0438, 0·0456	97·6	0·0460, 0·0466	101·4
	0·0916	0·0883, 0·0909	97·8	0·0888, 0·0897	97·5
Camp[17] ..	0·0916	— —	—	0·0671	73·3
Miscellaneous methods					
Pirrone[8]	0·0368	0·0426, 0·0422	115·2	Not applicable in the presence of lactose	

TABLE II*b*

RESULTS BY PUCHER'S METHOD

	Citric acid taken mg.	Extinction coefficient: Found	Extinction coefficient: Given by author
Pucher[10]	0·1	0·327	0·115
	0·5	1·057, 0·94	0·589
	1·0	1·653, 1·603	1·119

Gowing-Scopes[12] method the reagent* is reduced to metallic mercury, whereas in Pirrone's[8] method the lactose is charred by the rather large amount of concentrated sulphuric acid present. Rogina's method yields somewhat uncertain

* A mixture of mercuric nitrate, manganese nitrate and nitric acid.

results, as it is difficult to ascertain when sufficient potassium persulphate (which is used as an oxidising agent instead of potassium permanganate) has been added. Moreover, when lactose is present, shining plate-form crystals appear together with the normal amorphous precipitate.

Analysis of the various precipitates obtained in the mercury methods disclosed a possible general source of error—namely, the varying amount of mercury present —which casts considerable doubt on the validity of the factors (given by the various authors) used to calculate the weight of citric acid.

It will be realised, therefore, that taking 77 per cent. (as obtained in the test experiments) as the average content of mercury in the precipitate, the factor used by Beau would give only 92 per cent. of the citric acid present, whereas in the Gowing-Scopes method (85 per cent. average mercury-content) the yield would be only 86 per cent. Actually, we found the yield in the Beau method to be over 95 per cent. of the citric acid taken (Table II*a*), except in those experiments carried out on 0·0184 g. of citric acid where duplicate determinations gave results 55 per cent. and 68 per cent. of the theoretical. In the Gowing-Scopes test experiments the yield was approximately 84 per cent. of the theoretical. These criticisms refer to determinations made on pure citric acid.

The acetone methods have the disadvantage that they are somewhat lengthy, especially if lactose is present, and require continued attention from the analyst. The factors used are again empirical in some instances, and appear not to apply to all amounts of citric acid. Täufel and Mayr's method proved the most satisfactory in this group.

Pucher's method, which gave results rather different from those reported by the author, can only be used for very dilute solutions of citric acid. Thunberg's method was not considered, as the technique is subject to many errors; it is only applicable to quantities of citric acid of the order of 0·008 mg. per ml.

As a result of this preliminary survey of the possible methods, it was decided to investigate more fully the pentabromoacetone methods, which certainly have the advantage that they are specific for citric acid and acetone dicarboxylic acid. Moreover, acetone dicarboxylic acid, if present, is easily removed by addition of bromine prior to the oxidation of the citric acid. Preliminary tests proved these methods to be the most satisfactory when a large number of determinations have to be carried out.

[The paper by Täufel and Schoierer[34] was published after this work had been completed.]

(*c*) THE PENTABROMOACETONE METHOD.—Since the original Stahre[18]–Kunz[2] method was adapted by von der Heide[19] for the determination of citric acid in wine there have been a large number of modifications suggested by various workers, some of major import (especially those concerning the temperature of reaction), others minor in their significance. The following appear to be the most important: Hartmann and Hillig[20] (1927), Hartmann and Hillig[21] (1928), A.O.A.C.[22] (1930), Supplee and Bellis[23] (1921), McClure[24] (1922), Steuart[25] (1924), Bleyer and Schwaibold[26] (1925), Kometiani[27] (1931), Berg and Schulze[28] (1934), Reichard[29] (1934). The last-named studied the whole process thoroughly and embodied certain modifications in a revised method which he used for wine and later for fruit products, demonstrating

an accuracy within 1 mg. for amounts of citric acid between 5 and 100 mg. In 1934 Reichard[30] further showed that the presence of 5 g. of lactose in the reaction mixture did not interfere with the pentabromoacetone process, and the method was therefore applied by him to the analysis of milk and cheese.

As some of the methods are similar in character, only the most representative have actually been tested in the present investigation.

It is not proposed to describe the details of the various methods; they can be obtained by reference to the original papers. One or two stages were, however, standardised in order to make comparison possible:

(*a*) In all cases the use of asbestos was omitted, separation of the pentabromoacetone precipitate being effected by filtration through sintered glass crucibles (size 10 G.4), which are much more convenient than Gooch crucibles with asbestos.

(*b*) The weight of pentabromoacetone was found by difference between the weights of the crucibles before and after extraction with alcohol and ether. This method was also adopted in the trials of the Berg and Schulze and Kometiani techniques instead of the authors' iodimetric methods.

(*c*) Where no volume of citric acid solution was indicated by the various authors in their original papers 100 ml. were used.

The results obtained by the various methods are given in Table III.

Comments on the Methods.—On the whole the results (Table III) for the citric acid solution are low, especially by Berg and Schulze's method, and by Kometiani's method when lactose is present. Otherwise there are not very great differences between the results obtained by various methods.

In McClure's method the pentabromoacetone was obtained as an oil which, however, solidified on cooling; otherwise the precipitates were all crystalline.

As mentioned above, special attention was paid to the question of the temperature of reaction, as this is one of the main factors with which most modifications are concerned.

TABLE III

RESULTS OF DETERMINATIONS OF CITRIC ACID BY PENTABROMOACETONE METHODS

Method	Skimmed milk powder "M"; citric acid Per Cent.	Pure citric acid 0·0913 g.		Average yield Per Cent.	Pure citric acid 0·0913 g. with 2·7 g. lactose		Average yield Per Cent.
		g.	g.		g.	g.	
Lampitt and Bogod[1] ..	1·82	0·0861,	0·0862	94·3		0·0851	93·2
A.O.A.C.[22]	1·78	0·0845,	0·0832	91·7	0·0792,	0·0829	90·8
McClure[24]	1·78	0·0844,	0·0838	92·1	0·0833		91·2
Berg and Schulze[28] ..	1·83	0·0760,	0·0796				
			0·0735	87·2	0·0807		88·4
Kometiani[27]	1·50	0·0880,	0·0874	96·0	0·0771,	0·0755	80·5
Reichard[30]	1·72	0·0895,	0·0886	97·5	0·0857,	0·0855	93·9

When a number of determinations were to be made simultaneously, the heating of the solution to 48 to 50° C. was found to be inconvenient, as was also the control of the temperature at 5° C. in Reichard's[30] method and the cooling to 8° C. advocated by Lampitt and Bogod.[1]

The preliminary addition of bromine, which will remove, among other substances, acetone dicarboxylic acid, was not necessary, as in no case was any precipitate formed. This addition may be necessary in wine or fruit products. It was also concluded that when sintered glass crucibles are used the amount of washing stated by Hartmann and Hillig[20,21] is excessive. In Berg and Schulze's[28] method ammonium sulphate is added in order, so the authors state, to help clarify the solution and to prevent the oxidation going too far and proceeding too vigorously. It was found, however, that the rate of oxidation was very considerably retarded, and in the test experiments the ammonium sulphate appeared to be unnecessary.

The rate of reaction in Reichard's[30] method is very slow, and, to avoid too great an excess at any time, the permanganate had to be added very gradually. Here also the use of potassium bromide in place of ferrous sulphate for the final clarification of the solution is undesirable, as the pentabromoacetone formed is rather orange-coloured, possibly owing to the presence of absorbed bromine. The low results by the A.O.A.C. method are attributable to the fact that the reaction mixture is not cooled below room temperature before filtration, while in Kometiani's method the period of standing is short and the amount of bromide added rather low.

There are obviously many factors that can influence the final figure, and in a series of experiments a study was made of these variants. The method described later (see paragraph "*Method*," p. 662), was taken as a basis for experimental purposes, the points particularly studied being:

1. The effect of the volume of the original citric acid solution.
2. The effect of temperature for oxidation—48 to 50° C. or room temperature.
3. The method of addition of permanganate, the effect of excess, and the time for which the oxidation should proceed.
4. The treatment after oxidation.
5. The method of treatment after addition of ferrous sulphate.
6. The effect of excessive washing.
7. The possible correction for the solubility of pentabromoacetone.

The results are given in Table IV (p. 660).

It may be concluded from the results obtained that:

(1) There is no important difference between the results whether 50 ml. or 100 ml. of original citric acid solution are taken for analysis, but, owing to the solubility of pentabromoacetone (see below), it is advisable to keep the volume of the reaction solution as low as possible.

(2) The temperature of oxidation is immaterial (below 50° C.), but at lower temperatures a longer reaction time is necessary.

(3) Too rapid addition of permanganate is harmful, but excess does not matter; more ferrous sulphate solution, however, is then necessary.

(4) It is advisable to cool the reaction mixture in the ice-chest overnight before filtration.

(5) The volume of wash water should be kept as low as possible—not more than 25 ml.

TABLE IV

Method of treatment	Citric acid taken g.	Citric acid found g.	Average yield Per Cent.
1. *Effect of volume of citric acid solution*			
(*a*) Initial volume 50 ml.	0·0916	0·0887, 0·0885	96·7
(*b*) ,, ,, 50 ,, ...	0·0913	0·0887, 0·0884, 0·0888	97·1
(*c*) ,, ,, 100 ,, ...	0·0916	0·0886, 0·890	96·9
2. *Temperature of oxidation*			
(*a*) 48–50° C.	0·0916	0·0887, 0·0885	96·7
(*b*) Room temperature, cooled to 8°C. immediately after addition of permanganate	0·0916	0·0775, 0·0782	86·0
(*c*) At room temperature for 1 hour and then 16 hours after clarification	0·0916	0·0883, 0·0891	96·8
	0·0913	0·0883, 0·0884	96·9
3. *Permanganate treatment*			
(*a*) At 48–50° C.; 25 ml. $KMnO_4$ added all at once	0·0913	0·0810, 0·0806	88·5
	0·0916	0·0832, 0·0820	90·1
(*b*) Ditto, but $KMnO_4$ added dropwise	0·0916	0·0887, 0·0885	96·7
(*c*) At 48–50°; $KMnO_4$ added dropwise till separation of brown precipitate (about 10 ml.) ..	0·0916	0·0873	95·4
(*d*) Twice as much $KMnO_4$ as in (*c*) ..	0·0916	0·0874	95·5
	0·0913	0·0887, 0·0880, 0·0884	96·4
(*e*) Room temperature; 1 hour contact; $KMnO_4$ as in (*d*).. ..	0·0916	0·0868, 0·0874	95·8
4. *Treatment after oxidation* (permanganate added at 48–50° till precipitation of MnO_2)			
(*a*) Standing until precipitate cleared, before cooling to 8° C. ..	0·0916	0·0890, 0·0890	97·0
(*b*) Cooling to 8° C. immediately ..	0·0916	0·0887, 0·0885	96·7
5. *Treatment after ferrous sulphate stage* (Oxidation with permanganate as in 4 (*b*).)			
(*a*) In ice-chest overnight	0·0913	0·0881, 0·0889	97·0
(*b*) At room temperature 1 hour ..	0·0913	0·0888, 0·0875	96·5
(*c*) At room temperature 16 hours ..	0·0913	0·0862, 0·0869	94·8

6. *Effect of excessive washing of precipitate*

Weighed precipitates washed with 100 ml. of cold water, added in 6 portions and allowed to run through crucible slowly, lost 2·3 and 2·4 mg., respectively, equal to 2·5 per cent. of the total weight of precipitate.

Solubility of Pentabromoacetone.—In their determinations of citric acid Hartmann and Hillig[20] reported losses equivalent to 1·7 mg. of citric acid per 100 ml. of reaction mixture. These losses they considered to be due to the solubility of pentabromoacetone (this substance was isolated in small quantity from their filtrates by ether extraction), and they therefore proposed that this amount be added to the results obtained. Later they[21] modified this by suggesting an empirical factor, and still later, subsequent to a slight modification of reagents, suggested an arbitrary formula,[31] which was recommended in the Journal of the A.O.A.C. for milk.

Reichard[29] studied this question, with the results shown in Table V.

TABLE V

SOLUBILITY OF PENTABROMOACETONE (Reichard)

Solvent 100 ml.	Weight of pentabromoacetone dissolved at 5° C. mg.	Weight of pentabromoacetone dissolved at 15 to 18° C. mg.
Water	19·2	52·5
10 per cent. sulphuric acid + 100 mg. of bromine	Nil	5

Reichard, therefore, suggested that the reaction should be carried out at 5° C. No other authors appear to have given this question of solubility any consideration.

It seemed desirable, therefore, to determine the solubility of pentabromoacetone in the various reaction liquids. With this object in view, the reagents were mixed in the usual proportions and shaken at intervals during ten days, the mixtures being kept in the refrigerator meanwhile. The solubility is recorded as the loss of weight found after filtering, washing and drying the undissolved substance. The results obtained were as follows:

TABLE VI

SOLUBILITY OF PENTABROMOACETONE

	Solubility per 100 ml.
Reaction liquid as obtained with pure citric acid	3·7, 5·0 mg.
Reaction liquid as obtained with milk serum (including lactose)	5·0, 5·0 ,,
Reaction liquid as obtained with milk serum (0·5 per cent. of lactic acid)	5·9, 4·6 ,,
Average	5 ,,

The solubility of pentabromoacetone in the reaction mixtures under the conditions stated is therefore 5 mg. per 100 ml. It will be noticed that this figure agrees with that found by Reichard for the sulphuric acid and bromine mixture at 15°–18° C. A correction of 5 mg. of pentabromoacetone per 100 ml. of reaction mixture should therefore be added to the results obtained by the method advocated.

RECOMMENDED PENTABROMOACETONE METHOD.—The following method is therefore recommended as being convenient and accurate for the determination of citric acid within the limits of the indicated experimental error:

Reagents required.—Sulphuric acid: 1 vol. conc. acid (sp.gr. 1·84) + 1 vol. water.

Potassium bromide solution: 37·5 per cent. w/v.

Potassium permanganate solution: 5 per cent. w/v.

Ferrous sulphate solution: 20 per cent. (crystals) w/v in 1 per cent. sulphuric acid.

Method.—To 50 ml. of the milk serum, prepared as described in the paper by Lampitt and Bogod,[1]* or other solution containing citric acid, are added 10 ml. of the sulphuric acid (if not already added in the preparation of the solution) and 5 ml. of potassium bromide solution. (Except for pure citric acid and milk serum, 10 ml. of freshly-prepared bromine water should also be added and any precipitate formed from acetone dicarboxylic acid filtered off after half-an-hour's standing.) Potassium permanganate solution is added dropwise from a burette with constant shaking until a brown precipitate persists, 10 ml. being required usually for 0·1 g. of citric acid and 25 ml. for a milk serum. The mixture is allowed to stand at room temperature for 1 hour, further addition of permanganate being made if the brown precipitate disappears. Sufficient ferrous sulphate solution is then added slowly till a pale yellow solution containing a white precipitate is obtained, and the mixture is cooled in an ice-chest overnight (16 hours).

The precipitate is removed by filtration through a sintered glass crucible (size 10G4), the reaction flask being washed out with the filtrate to remove the last traces of precipitate, and the washings passed through the crucible. The precipitate in the crucible is then washed with portions of 10, 10 and 5 ml. of cold water. The crucible is dried to constant weight in a vacuum desiccator (about 16 hours). The precipitate is dissolved out of the crucible with industrial spirit followed by 20, 10 and 10 ml. portions of ether. The crucible is again dried in the vacuum desiccator and weighed, the loss in weight being taken as pentabromoacetone.

$$\text{Citric acid (anhydrous)} = 0{\cdot}424\left(W + \frac{0{\cdot}005V}{100}\right),$$

where W represents the difference in weight of the crucible before and after treatment with industrial spirit and ether; V the original volume of filtrate from reaction mixture, less the total volume of washings.

The accuracy that may be obtained with this method is demonstrated by the figures given in Tables VII and VIII, for determinations carried out in the absence of, and in the presence of lactose (1·4 g.), respectively.

* 150 g. of milk heated to 50 to 60° C. in a 250-ml. graduated flask and 25 ml. of potassium oxalate solution (2 per cent.) added; contents of flask shaken; 20 ml. H_2SO_4 (1 : 1) added and contents of flask shaken; after cooling, 10 ml. of phosphotungstic acid solution added and contents made up to 250 ml.; after vigorous shaking, contents allowed to settle for 5 minutes and serum filtered from the precipitate.

TABLE VII

DETERMINATION OF CITRIC ACID BY THE MODIFIED PENTABROMOACETONE METHOD

(Citric acid alone)

Anhydrous citric acid taken g.	Anhydrous citric acid found g.
0·00916	0·0081
	0·0093
0·0275	0·0275
	0·0282
0·0458	0·0460
	0·0455
0·0550	0·0551
0·0641	0·0644
0·0825	0·0828
0·0916	0·0908
0·1374	0·1361

TABLE VIII

DETERMINATION OF CITRIC ACID BY THE MODIFIED PENTABROMOACETONE METHOD

(With lactose present)

Anhydrous citric acid taken g.	Anhydrous citric acid found g.	Anhydrous citric acid taken g.	Anhydrous citric acid found g.
0·0092	0·0073		
	0·0084	0·0641	0·0636
	0·0091		0·0631
0·0183	0·0166		
0·0275	0·0270	0·0733	0·0726
	0·0268		0·0723
0·0366	0·0360	0·0916	0·0910
0·0458	0·0450	0·1100	0·1099
0·0550	0·0544	0·1374	0·1324

From these results it is concluded that amounts of citric acid up to **0·11 gm.** may be determined, in the presence of lactose, to within 2 mg.

TABLE IX

DETERMINATION OF CITRIC ACID—REPRODUCIBILITY OF RESULTS

(In the presence of lactose)

Citric acid taken g.	Citric acid found g.	Citric acid taken g.	Citric acid found g.
0·0183	0·0175	0·0733	0·0714
	0·0179		0·0716
	0·0177		0·0714
	0·0179		0·0715

Determination of known amounts of citric acid added to milk powder.—Citric acid determinations were carried out on "solutions" of milk powder to which known amounts of citric acid were added. The solutions were clarified as described by Lampitt and Bogod.[1] These results are shown in Table X.

TABLE X

DETERMINATION OF CITRIC ACID IN MILK

	Results obtained Per Cent.	Average Per Cent.	Added acid found Per Cent.
Original milk powder	1·83, 1·84, 1·85	1·84	—
Ditto + 0·18 per cent. citric acid	2·00, 1·94	1·97	0·13
Ditto + 0·46 per cent. citric acid	2·28, 2·27	2·28	0·44
Ditto + 0·92 per cent. citric acid	2·73, 2·76, 2·77	2·75	0·91

PART III

THE COMPOSITION OF THE PRECIPITATE OBTAINED IN THE PENTABROMOACETONE METHOD.

It is usually assumed that the precipitate obtained in the Stahre–Kunz process is pentabromoacetone. An examination has been made of the precipitate formed in the solution during the determination of the citric acid present in milk powder and in pure citric acid solutions.

These precipitates were formed in the usual way, using the normal volumes of reagents and washing with water only, and were dried to constant weight in a vacuum desiccator before analysis.

Bromine was determined by the Stepanow method.[33]

TABLE XI

COMPOSITION OF THE PENTABROMOACETONE PRECIPITATE

	Precipitate from milk serum	Precipitate from pure citric acid
Melting-point	72 to 73° C.	71 to 72° C.
Bromine-content, per cent. .. (theory, 88·3 per cent.)	85·8, 85·5, 86·1	86·6, 85·5, 86·8

Beilstein gives figures of 72·8 to 76° C. for the melting-point reported by various observers; Mulliken, *Identification of Organic Compounds*, gives 76° C.; Richter's *Organic Chemistry* gives 74° C. Reichard[29] found 71 to 72° C. for the crude product and 73° C. for the crystallised material. Steuart[25] found that his pentabromoacetone had melting-point 72 to 75° C. and bromine-content by Stepanow's method 88·0 per cent.

From the results it is concluded that the precipitate obtained from milk serum is essentially identical with that from pure citric acid solution, and that both are pentabromoacetone.

SUMMARY.—1. Citric acid has been isolated in crystalline form from milk powder.

2. The methods available for the determination of citric acid have been discussed and the majority tested experimentally.

3. Not all of the methods are applicable to the determination of citric acid in presence of lactose without previous treatment.

4. In the modifications of Denigès' method, the numerical factors proposed by the various authors were not applicable to all concentrations of citric acid, and were found to be incorrect in some cases.

5. Acetone methods were lengthy and not reliable. They appear to be somewhat empirical.

6. It was decided that the pentabromoacetone method was the most convenient, and was deemed worthy of study. The various modifications published have been reviewed.

7. The point on which the opinions of previous authors have most differed is the temperature at which the reaction should be conducted. This question, amongst others, has been studied and a technique evolved which is capable of yielding results of a high degree of accuracy. The results were less than 2 mg. low for weights of citric acid up to 0·11 g. in the presence of milk serum.

8. The precipitate formed has been shown to be pentabromoacetone: the solubility was 5 mg. per 100 ml. of reaction liquid at 0° C.

In conclusion, we desire to thank Messrs. J. Lyons & Co., Ltd., in whose laboratories the work was conducted, for permission to publish this paper.

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The Estimation of the Original Freezing-point of Sour Milk

By H. J. EVANS, B.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, April* 4, 1936)

It is almost universally agreed that the osmotic pressure of the serum of fresh milk is the one property of milk which is almost constant, and that the smallest osmotic pressure of genuine milk ever observed is represented by a freezing-point depression of about 0·53° C., as determined by the Hortvet method. The average depression obtained by different observers varies from 0·54° to 0·55° C. If, therefore, a fresh milk gives a freezing-point depression of less than 0·53° C., it is definite proof of the presence of added water.

This constant osmotic pressure is due to the combined effects of three of the components of the milk serum, *viz.* (i) the lactose; (ii) the salts of potash and soda; (iii) the salts of lime and magnesia.

An equilibrium is maintained between these components. That is to say, any fall in the lactose-content is at once balanced by a rise in one or both of the other components until equilibrium is again reached.

Considering first of all the influence of the three components mentioned, it has been calculated by Coste and Shelbourn[1] that the osmotic pressure in a normal milk is derived somewhat as follows (osmotic pressures being represented by freezing-point depressions):

Lactose	0·25°	} 0·36°
Salts of potash and soda ..	0·11°	
Salts of lime and magnesia ..	0·20°	
Total ..	0·56°	

Thus in a normal milk which gives a freezing-point depression of 0·56° C., about two-thirds of this depression is brought about by the combined effect of the lactose and the salts of potash and soda, and one-third by those salts of lime and magnesia which are in solution.

The only component of milk which is destroyed by fermentation, and which cannot be recovered, is the lactose. An accurate analysis of the sour milk can, however, be made, and the amount of lactose in the original milk can be estimated therefrom. The major portion of the salts of potash and soda can be recovered from the ash. If, therefore, we take a weight of the sour milk equivalent to 50 ml. of the fresh milk, ash it, dissolve the ash in water, add to the solution the amount of lactose* originally present in 50 ml. of the fresh milk, and make up to the original volume, less the volume occupied by the fat, we have a solution which should give a freezing-point depression approximating to that of the original milk deprived of its lime and magnesia compounds, because the latter have been rendered almost completely insoluble by ignition.

The problem of estimating the original freezing-point of the milk then seems to resolve itself into that of bringing the lime and magnesia compounds back

* In the experiments described later the lactose added was the monohydrate; its purity, polarimetrically determined, was 100·3 per cent.

into approximately the same state of solution as that in which they existed in the original milk.

It is well established that the lime and phosphorus compounds occurring in fresh milk are not in perfect solution, but are partly in solution and partly in colloidal suspension. According to Van Slyke and Bosworth,[2] about 53 per cent. of the total phosphorus and 35 per cent. of the total calcium are in solution, the remainder being associated with the proteins, etc. It would, therefore, seem necessary to treat the ash in such a way as to bring into solution about one-half of the total phosphorus and one-third of the total lime.

The ash of a normal milk was prepared as follows: Twenty-five ml. were ignited at a very low temperature to a black char. This was extracted with water, and the residual carbon was completely burnt. The extract was added to this, and the whole was evaporated and again ignited at a very low temperature. This yielded 0·203 g. of ash ≡ 0·786 per cent. on the milk taken. It was found that the lime portion of this ash was almost insoluble in water and in acetic acid. The whole of the ash, however, dissolved completely in hydrochloric acid, and when the solution was taken down to dryness the residue was completely soluble in water. The resultant solution, however, contained a large quantity of free hydrochloric acid. To remove this, excess of ammonia was added, and the whole was evaporated to dryness and very cautiously heated until white fumes of ammonium chloride were no longer given off. The residue was then treated with acetic acid, evaporated to dryness, and heated in the water-oven until excess of acetic acid was completely removed. It was then extracted with water, when a portion, weighing 0·048 g. (23·6 per cent. of the total ash), remained insoluble. This had the following composition:

Calcium, as CaO	0·026 g. = 12·8 per cent. of the ash	= 23·6 per cent.
Phosphorus, as P_2O_5	0·022 g. = 10·8 ,, ,, ,, ,, ,,	

which corresponds with the formula $Ca_3(PO_4)_2$.

The soluble portion contained the following:

Calcium, as CaO	0·017 g. = 8·4 per cent. of the ash	Intermediate between $CaH_4(PO_4)_2$ and $CaHPO_4$
Phosphorus, as P_2O_5	0·031 g. = 15·3 ,, ,, ,, ,, ,,	

The total calcium (as oxide) determined separately was 21·7 per cent.

,, ,, phosphorus as P_2O_5 ,, ,, ,, 26·4 ,, ,,

From these figures it is seen that of the total calcium present, 39 per cent., and of the total phosphorus, 58 per cent., were soluble in water after the above treatment. This corresponds closely with the conditions existing in fresh milk with respect to calcium and phosphorus as observed by Van Slyke and Bosworth.[2]

The ash of a normal milk was weighed, treated with hydrochloric acid, ammonia and acetic acid as described, and weighed again. The gain in weight was of the order of 2 to 3 per cent. of the weight of the ash, which would be accounted for by the formation of acid calcium phosphates. It was, therefore, decided to treat the ash in the foregoing manner, the whole process of estimation of the freezing-point being as follows:—

PROCEDURE: A full analysis of the sour milk is made by the Government Laboratory process, and the figures for fat and non-fatty solids in the fresh milk

are thus obtained. In addition to this, the ash and proteins are determined, and, by subtracting the sum of these from the non-fatty solids figure, the percentage of lactose in the fresh milk is calculated.

Alternatively, the amount of lactose in the original milk could be found by determining that in the sour milk, and correcting the amount so found by the usual method of the Government Laboratory.[3]

From the figures for fat and non-fatty solids the gravity of the original milk is obtained, and a quantity equivalent to 50 ml. is weighed out, evaporated to dryness, and carefully ignited at a very low temperature to a black char. It is then taken up with hydrochloric acid,* again evaporated to dryness and taken up with water. Excess of ammonia is added, and the whole is again evaporated to dryness, the carbonaceous mass being rubbed down to a fine powder while still moist. The whole is then gently heated in the mouth of a muffle until all white fumes of ammonium salts have been driven off.

The residue, which is slightly alkaline at this stage, is brought into a neutral condition by being taken up with 10 per cent. acetic acid, evaporated to dryness, and heated in the water-oven for several hours until all traces of acetic acid have been removed. It is then taken up with about 30 ml. of cold water, and the requisite amount of $N/10$ citric acid solution is added to bring the reconstituted serum to the correct acidity as indicated by the N.F.S. figure (*cf.* Note, p. 670). The calculated amount of lactose for 50 ml. is also added, and the whole is made up to a volume of 50 ml., less the volume occupied by the fat. The freezing-point is then taken.

A number of samples of milk were treated in this way, and the following Table gives the results in detail:

TABLE

ORIGINAL MILK

Milk No.	Source	Fat Per Cent.	Lactose Per Cent.	Protein Per Cent.	Ash Per Cent.	Total N.F.S. Per Cent.	Acidity, ml. of $N/10$ soda per 10 ml.	F.pt. °C.
1	Purchased from dealer ..	3·59	4·82	3·29	0·78	8·89	1·8	0·535
2	Purchased from dealer ..	3·71	4·86	3·40	0·78	9·04	1·9	0·540
3	Milk mixed with equal quantity of normal saline solution	1·92	2·51	1·75	0·86	5·12	1·0	0·530
4	Mixed sample	3·28	4·89	3·20	0·81	8·90	1·7	0·530
5	Purchased from dealer ..	3·29	4·91	3·14	0·76	8·81	1·6	0·547
6	Sample submitted ..	3·30	4·62	3·18	0·71	8·51	1·5	0·531
7	Mixed sample	3·01	4·64	3·18	0·70	8·52	1·5	0·535
8	Farmer's sample	3·50	4·98	3·41	0·76	9·15	1·9	0·550
9	Mixed sample	3·25	4·62	3·30	0·74	8·66	1·6	0·545
10	Mixed sample	3·39	4·76	3·26	0·73	8·75	1·7	0·548
11	Farmer's sample	3·08	4·88	3·57	0·75	9·20	1·8	0·555
12	Mixed milk for information	3·90	4·81	3·13	0·76	8·70	not known	0·546
13	Mixed milk	3·45	4·94	3·07	0·79	8·80	,, ,,	0·545
14	Mixed milk	3·70	4·95	3·21	0·84	9·00	,, ,,	0·549
15	Adulterated sample ..	2·69	4·59	2·83	0·66	8·08	1·75	0·483
16	Adulterated sample ..	2·43	3·53	2·30	0·55	6·38	1·00	0·390

* Acetic acid cannot be used at this stage in place of hydrochloric acid, because the ignited calcium phosphate cannot be dissolved in the former, irrespective of the strength used.

Sour Milk

Milk No.	Source	Calculated sp.gr.	Weight of sour milk taken g.	Lactose added g.	N/10 Citric acid added ml.	Volume made up to ml.	Acidity, ml. of N/10 soda per 10 ml.	F.pt. °C.
1	Purchased from dealer ..	1032	51·60	2·410	9	48·0	1·7	0·534
2	Purchased from dealer ..	1033	51·65	2·430	9	48·0	1·8	0·530
3	Milk mixed with equal quantity of normal saline solution	1018	50·90	1·250	5	48·9	1·0	0·535
4	Mixed sample	1033	51·65	2·450	9	48·2	1·9	0·538
5	Purchased from dealer ..	1032·5	51·63	2·455	8	48·3	1·7	0·540
6	Sample submitted	1031·5	51·58	2·310	8	48·2	1·7	0·533
7	Mixed sample	1031·5	51·58	2·320	8	48·4	1·6	0·530
8	Farmer's sample	1034	51·70	2·490	9	48·1	1·8	0·540
9	Mixed sample	1032	51·60	2·310	8	48·2	1·7	0·538
10	Mixed sample	1032	51·60	2·380	8	48·2	1·6	0·540
11	Farmer's sample	1034	51·70	2·440	9	48·4	1·9	0·547
12	Mixed milk for information	1031·5	51·57	2·405	8·5	47·9	1·7	0·535
13	Mixed milk	1033	51·65	2·470	9	48·1	1·8	0·541
14	Mixed milk	1033	51·65	2·475	9	48·0	1·9	0·530
15	Adulterated sample ..	1030	51·50	2·295	8	48·5	1·6	0·473
16	Adulterated sample ..	1023·5	51·18	1·765	5	48·7	1·1	0·393

Comparison of Figures for Freezing-points of Fresh Milks and Calculated Freezing-points of Corresponding Sour Milks

No.	Freezing-point of fresh milk °C.	Freezing-point of corresponding sour milk °C.	Difference
1	0·535	0·534	−0·001
2	0·540	0·530	−0·010
3	0·530	0·535	+0·005
4	0·530	0·538	+0·008
5	0·547	0·540	−0·007
6	0·531	0·533	+0·002
7	0·535	0·530	−0·005
8	0·550	0·540	−0·010
9	0·545	0·538	−0·007
10	0·548	0·540	−0·008
11	0·555	0·547	−0·008
12	0·546	0·535	−0·011
13	0·545	0·541	−0·004
14	0·549	0·530	−0·019
15	0·483	0·473	−0·010
16	0·390	0·393	+0·003

Of these results, Nos. 3, 12, 13, and 14 are of special interest. No. 3 was an artificially-prepared "Abnormal" milk obtained by mixing equal volumes of a fresh milk and physiologically normal saline solution.

Nos. 12, 13 and 14 were supplied by Mr. G. D. Elsdon, for whose help and co-operation I wish to express my best thanks. He analysed these milks and determined their original freezing-points, and kept them until they were in a sour condition before passing them on to me. He also gave me his figures for the fat and non-fatty solids.

The following modification of the method previously detailed was used for Nos. 15 and 16. The milk was evaporated to dryness and very gently ignited (*cf.* p. 668). The char was then extracted with 15 per cent. hydrochloric acid, the extract filtered, and evaporated, and the residue completely ashed. The extract was added to this, and the whole was evaporated to dryness and taken up with a little water. Excess of ammonia was added to this solution, the whole was again evaporated to dryness and very gently heated until white fumes of ammonium chloride were no longer given off, and the process completed as before.

The advantages of this modification appear to be that both the ignition and the removal of the ammonium salts can be carried out at the same time and at lower temperatures than usual.

In conclusion I wish to tender my thanks to my chief assistant, Mr. R. K. Matthews, F.I.C., for helpful suggestions, and to Mr. Henry Davies, B.Sc., for assistance in carrying out the analyses.

NOTE ON THE ESTIMATION OF THE ACIDITY OF THE ORIGINAL MILK.—This has been arrived at by a purely empirical method. It has been generally observed that the natural acidities of fresh milks seem to be proportional to the N.F.S. figures. The figures for N.F.S. of various milks examined have been plotted against the acidities determined, and from this curve the original acidity of the milk has been deduced.

Non-fatty solids Per Cent.	Acidity
6·16	0·80
6·52	1·00
7·79	1·40
8·36	1·60
8·44	1·65
8·50	1·70
8·75	1·80
9·00	1·90

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ANALYTICAL LABORATORY
9A, THE TEMPLE
DALE STREET, LIVERPOOL, 2

The Determination of Boric Acid in Dried Fruit

By W. BURNS BROWN, M.Sc., A.I.C.

The occurrence of boric acid in dried fruit (sultanas, raisins and currants) has been reported from time to time. Rudd Thompson[1] states that boric acid in fruit cake is present mainly in the dried fruit. A summary of reports on the natural occurrence of boric acid is given by Scott Dodd,[2] who also determined the natural boric acid content of a number of fruits and vegetable products.[3] In dried fruit the amount varies between 100 and 220 p.p.m. It has been suggested recently that the boric acid content of dried fruit from certain sources is very much higher—of the order of 2000 parts per million, and that it does not occur naturally, but is largely, if not wholly, due to special treatment. These suggestions cannot be passed without investigation.

Boric acid in dried fruit is always determined by some modification of the volumetric method of Thomson,[4] but there have been differences of opinion with regard to details of procedure. I have examined these details and checked the method, using the Rosenbladt–Gooch gravimetric method[5] as an ultimate standard.

Purity of the Boric Acid used.—This has been determined volumetrically, the mean of several titrations giving the purity as 100·2 per cent., and gravimetrically by the Rosenbladt–Gooch method,[5] which gave results of 100·5 and 99·8 per cent. The sample was assumed to be of 100 per cent. purity.

Conditions Required for the Volumetric Determination.—The original method of Thomson[4] has been modified and standardised for different purposes by the Government Laboratory,[6] by the Association of Official Agricultural Chemists,[7] and by Scott Dodd.[8,9] These modifications have been studied.

(i) *Removal of Phosphates.*—This is usually effected by adding calcium chloride solution and making alkaline with sodium hydroxide solution. Loss of boric acid may occur during this operation, possibly by adsorption on the precipitate of calcium phosphate. The amount of phosphate extracted with the boric acid from a sample of Australian sultanas was determined. It was separated by precipitation as ammonium phosphomolybdate, re-dissolved, and precipitated with magnesia mixture. The precipitate was collected on a Gooch crucible, ignited, and weighed as magnesium pyrophosphate, $Mg_2P_2O_7$. The amount of phosphate calculated as P_2O_5 was 0·03 per cent.

The best conditions for the removal of phosphate without loss of boric acid have been determined. Portions of a solution of boric acid were pipetted into 100-ml. calibrated flasks, and to each was added a volume of sodium phosphate solution, equivalent to 8 mg. of phosphoric anhydride. This corresponds to the phosphate extracted from the 25 g. of fruit upon which the determination is usually made. Either 1 or 5 ml. of a 10 per cent. solution of calcium chloride ($CaCl_2.6H_2O$) and 0·2 ml. of 1 per cent. phenolphthalein solution were added, and then *N* sodium hydroxide solution, drop by drop, until the solution was faintly pink. This is the alkalinity generally recommended, but in a number

of experiments either 0·1 ml. or 1·0 ml. of *N* sodium hydroxide solution was added in excess. The whole was diluted to the mark, the precipitated phosphate was separated on a dry filter, and 75 ml. of the filtrate were collected in a conical flask. After the addition of 0·1 ml. of "Sofnol No. 1" (1·2 g. per litre of alcohol) the solution was acidified with *N* sulphuric acid until the pink colour of the indicator was shown. The solution was boiled for 1 minute and cooled, and after a further addition of 0·2 ml. of phenolphthalein solution, it was titrated with 0·05 *N* sodium hydroxide solution until the end-point of "Sofnol No. 1" was reached, after which 1 g. of mannitol was added and the titration continued to the end-point of phenolphthalein.

The boric acid actually present in the portions taken was determined by titration of the same volume of solution without addition of phosphate or calcium chloride. Five and 25 mg. of boric acid correspond with 200 and 1000 p.p.m., respectively, in a determination on 25 g. of fruit. The results are given in Table I.

TABLE I

Boric acid present mg.	Calcium chloride (10 per cent. solution) added ml.	Ratio CaO/P_2O_5	Boric acid found when using the undermentioned volume of *N* NaOH in excess		
			0·0 ml. mg.	0·1 ml. mg.	1·0 ml. mg.
4·9	1	2·8	6·5	4·9	4·8
	1		6·2	4·9	4·7
	5	14	5·1	4·5	4·6
	5		5·2	4·7	4·6
24·4	1	2·8	25·2	24·4	24·0
	1		25·2	24·4	24·0
	5	14	24·6	24·0	23·8
	5		24·5	24·2	23·6

If the solution was made just alkaline to phenolphthalein high results were obtained, owing to incomplete precipitation of the phosphates. With a large excess of alkali there was a slight loss of boric acid, which was increased when a greater excess of calcium chloride was used. The larger proportion of calcium chloride (14 times the theoretical amount required to precipitate all the phosphate present) made the removal of phosphates more complete when the solution was only sufficiently alkaline to be faintly pink. The most accurate results were obtained when 1 ml. of calcium chloride solution was used and the alkalinity increased by adding 0·1 ml. of *N* sodium hydroxide after the first pink colour of phenolphthalein had been reached. Since the amounts of boric acid found varied considerably at this point, it is advisable, when the amount of phosphate present is uncertain, to add rather more sodium hydroxide solution, say 0·2 ml.

In the determination of boric acid in dried fruit, lime water was added before the final ashing. The amount of calcium added in this form was equivalent to about 1 ml. of the 10 per cent. solution of calcium chloride ($CaCl_2.6H_2O$). Most of this calcium was present in the extract, but, to ensure complete removal of phosphates, 1 ml. of the calcium chloride solution was added before making the liquid alkaline. The loss of boric acid caused by the presence of this increased excess of calcium is unlikely to exceed 1·5 per cent.

If a porcelain basin is used for charring dried fruit made alkaline with sodium hydroxide, some silica and aluminium are extracted. On the addition of dilute acid and filtration, the filtrate will contain the aluminium and a large part of the silica as colloidal silicic acid. In the removal of the phosphates, aluminium hydroxide and calcium silicate are also thrown down as a voluminous precipitate. Loss of boric acid in this precipitate may be appreciable, and determinations carried out in porcelain basins might be expected to give lower results than those obtained in platinum basins. In general, the use of porcelain basins gives the higher results, the loss being masked by the effects due to incomplete charring or to the presence of unprecipitated silicic acid (see later).

(ii) *Removal of carbon dioxide and determination of the alkali used in blank experiments.*—A conical flask is most convenient for boiling, cooling and titrating the solution. The necessary time of boiling in a 250-ml. conical flask has been determined (see Table II). To certain of the solutions of boric acid were added 10 ml. of either 0·1 *N* or *N* sodium carbonate solution. The liquid was diluted to 75 ml., and acidified with *N* sulphuric acid before boiling. For the subsequent titration with phenolphthalein as the final indicator, 0·05 *N* sodium hydroxide solution is used. One g. of mannitol is added.

TABLE II

Preliminary indicator	Na_2CO_3 soln. added	Boric acid found after different periods of boiling		
		1 min.	5 min.	10 min.
"Sofnol No. 1"	None	61·6	61·7	61·4
	10 ml. 0·1 *N*	61·7	61·4	61·4
	10 ml. *N*	61·4	61·5	61·3
Methyl orange	None	61·4		
	10 ml. *N*	61·7		
"Sofnol No. 1"	None	6·3	6·3	6·3
	10 ml. 0·1 *N*	6·5	6·3	6·3
	10 ml. *N*	6·5	6·4	6·4
Methyl orange	None	6·2		
	10 ml. *N*	6·3		

On acidification, the solution containing 10 ml. of *N*-sodium carbonate effervesces strongly in the cold, and is therefore saturated with carbon dioxide. It will be seen that one minute's boiling is sufficient. Rapid cooling is unnecessary, as was shown when determining the amount of sodium hydroxide used in a blank experiment. Seventy-five ml. of distilled water were acidified with 0·1 ml. of *N* sulphuric acid, boiled for 1 minute, cooled and titrated with 0·05 *N* sodium hydroxide solution. Either 0·1 ml. of 0·02 per cent. methyl orange solution or 0·1 ml. of the solution of "Sofnol No. 1" was added as preliminary indicator, and 0·4 ml. of 1 per cent. phenolphthalein solution as final indicator. Since the end-point to phenolphthalein is fleeting, it was taken arbitrarily as the point at which the solution remained pink for half-a-minute. Between the "Sofnol No. 1" and phenolphthalein end-points, 0·10 ml. of 0·05 *N* sodium hydroxide was used. This was not altered when a 15-minute interval was allowed between cooling and

beginning the titration, or when there was a 5-minute interval after the first end-point was reached. The corresponding figure with methyl orange was 0·17 ml. In fact, the solution absorbed atmospheric carbon dioxide only when nearing the phenolphthalein end-point. These figures were confirmed electrometrically. The volume of 0·05 *N* sodium hydroxide solution required to alter the *p*H of the solution from 4·4 (the methyl orange end-point) to 6·0 (the "Sofnol No. 1" end-point) was thus 0·07 ml., which was about the amount to be expected at a dilution of 75 to 100 ml. The volume required to change the *p*H from 6·0 to 8·3 (the phenolphthalein end-point) was 0·1 ml., which must mainly have been used in neutralising the absorbed carbon dioxide. These allowances were made throughout. The addition, at the end of the titration, of a further quantity of glycerol or mannitol involves shaking and should be avoided, since the carbon dioxide absorbed during this process itself discharges the colour of the phenolphthalein, and necessitates a further addition of 0·03 to 0·07 ml. of 0·05 *N* alkali. For more accurate work the complete exclusion of carbon dioxide is desirable, and a special titrating vessel, such as that described by Jackson,[10] should be employed.

The standard alkali must be free from carbonate. It is best prepared as recommended by Pregl.[11] A closed burette system should be employed. All reagents must be free from boric acid. Alkaline solutions readily extract borate from boro-silicate glass, *e.g.* Pyrex, and alkaline reagents should not be left in contact with this glassware.

(iii) *Effects of different indicators and of glycerol and mannitol.*—Scott Dodd[8,9] prefers "Sofnol No. 1" to the methyl orange used by other chemists. When determining amounts of boric acid up to 62 mg. (Table II) the same results are given with each indicator, but "Sofnol No. 1" gives a sharper end-point, and with the extract from dried fruit it minimises any error due to incomplete charring. Results obtained with glycerol and with mannitol were the same, but mannitol is more convenient to handle, and does not increase the volume of the final solution. One g. of mannitol is sufficient for amounts of boric acid up to 62 mg.

Extraction of Boric Acid: Importance of Complete Charring.—Thorough charring of the fruit before extraction is universally recommended, but no criterion of completeness is given. If charring is incomplete, the extract contains weak organic acids, produced during charring, which are returned as boric acid when this is determined volumetrically. If "Sofnol No. 1" is used, the effect is much less than with methyl orange, with which the error may amount to several times the quantity of boric acid present. The source of these acids is probably the sugars, of which there are about 70 per cent. in the fruit. The following experiments show that absence of colour from the extract is not a criterion of satisfactory charring. Ten g. of sucrose with 10 ml. of *N* sodium hydroxide solution were evaporated in a porcelain basin and charred. The char was acidified with *N* hydrochloric acid, the extract filtered into a 100-ml. flask, and the residue washed with hot water. As when dealing with fruit, 1 ml. of 10 per cent. calcium chloride solution was added, followed by *N* sodium hydroxide solution, 0·1 ml. in excess of the volume required for the end-point of phenolphthalein. The solution was diluted to the mark and filtered through a dry paper. The small loss of solution on the paper and in the precipitate was neglected. The colour of the

filtrate was compared, in 100-ml. Nessler glasses, with solutions containing known amounts of 0·1 *N* potassium dichromate solution. The filtrate was then divided into two equal parts, each of which was acidified with *N* sulphuric acid, boiled for 1 minute and cooled. To one part was added 0·1 ml. of methyl orange, and to the other 0·1 ml. of "Sofnol No. 1," and each was titrated with 0·05 *N* sodium hydroxide solution from the turning point of each indicator to that of phenolphthalein. Neutral mannitol does not affect the titration. A similar experiment (No. 11) was made in a platinum basin with very thorough charring, most of the carbon being burnt away. The usual corrections for titration blanks were applied. The results are shown in Table III.

It will be seen that: (1) The effect of incomplete charring is much greater when using methyl orange than when using "Sofnol No. 1," particularly when the extract is distinctly coloured. (2) When the sugar was very carefully charred in a porcelain basin (Expt. No. 10), the final titrations corresponded with 35 p.p.m. of boric acid when methyl orange was used, and 20 p.p.m. with "Sofnol No. 1." (3) The thorough charring which is possible in a platinum basin completely destroys all traces of organic acids.

TABLE III

Expt.	Colour of solution	0·1 *N* $K_2Cr_2O_7$ soln. to give equivalent colour ml.	Titration of half the extract, 0·05 *N*-NaOH used		Apparent boric acid if extract were obtained from 25 g. of fruit	
			Methyl orange ml.	"Sofnol No.1" ml.	Methyl orange p.p.m.	"Sofnol No. 1" p.p.m.
1	Pale orange	1·2	5·6	0·45	1350	100
2	Pale yellow	0·7	4·1	0·35	980	85
3	,, ,,	0·5	2·1	0·25	500	60
4	Almost colourless	0·2	1·0	0·20	240	50
5	,, ,,	0·2	0·83	0·22	200	50
6	,, ,,	0·2	—	0·18	—	45
7	Colourless	0·05	0·31	0·17	75	40
8	,,	0·05	0·33	0·15	80	35
9	,,	0·05	0·28	0·10	70	25
10	,,	0·05	0·14	0·09	35	20
11	(Platinum basin) colourless	0·05	0·00	0·00	0	0

The sharpness of colour-change of the preliminary indicator is a valuable indication of the accuracy of a determination. With "Sofnol No. 1" the volume of 0·05 *N* sodium hydroxide required to change the colour from bright red to clear yellow should be less than 0·1 ml. If more is necessary, either charring has been incomplete, or phosphates have not been completely removed, and the titration will indicate an amount of boric acid greatly in excess of the true content.

The silicate present in the extract when a porcelain basin is used may not be completely precipitated with the phosphates. In a blank experiment carried through in a porcelain basin, starting with 10 ml. of 2 *N* sodium hydroxide solution, a small titration result between the end-points of "Sofnol No. 1" and phenolphthalein was obtained, corresponding with 15 p.p.m. in a determination on 25 g.

of material. It was unaffected by the addition of mannitol, and could not be due to boric acid extracted from the basin. It was probably caused by a trace of silicic acid not precipitated by calcium chloride. It is possible to obtain a zero result after charring sucrose in a platinum basin (Expt. No. 11, Table III). This blank may account for a large part of the titration to "Sofnol No. 1" in experiment 10. No correction has been made in determinations on dried fruit, since it is not certain that it would apply under the different conditions of charring.

Thus, a platinum basin must be used if the highest accuracy is required. The preliminary charring is then more easily carried out, but it must be carefully done, the charred mass being removed, crushed in a glass mortar, and returned to the basin for further heating before extraction. The final ashing proceeds more rapidly when the residue from the preliminary charring is made alkaline with lime water instead of sodium hydroxide. For most purposes careful charring in a porcelain basin is satisfactory. Table IV shows results obtained by different methods upon a sample of South African raisins. The difference between the boric acid content as determined with the use of a porcelain basin and that obtained with a platinum basin was only 5 p.p.m. when "Sofnol No. 1" was employed.

TABLE IV

Type of basin	Method of determination	Boric acid p.p.m.
Platinum	Volumetric; titration from methyl orange end-point ..	110
	titration from "Sofnol No. 1" end-point ..	105
Porcelain	Electrometric; titration from *p*H 4·4 (methyl orange end-point)	130
	titration from *p*H 6·0 ("Sofnol No. 1" end-point)	110
Platinum	Gravimetric	120

ELECTROMETRIC TITRATIONS.—Porcelain basins were used for the charring in these experiments. The hydrogen ion concentration, after each addition of sodium hydroxide, was determined by using a pair of electrodes of the type described by Hildebrand,[12] with Poggendorf's potentiometric system. In general, the two electrodes give identical readings. The results are shown in Table V and graphically in Fig. 1. The *p*H values taken as corresponding with the indicator end-points were the averages of several determinations. The usual allowances were made for the volume of sodium hydroxide required in blank experiments. In Expt. 1 the addition of 1 g. of mannitol was made just before the phenolphthalein end-point, whilst in Expts. 2 and 4 the mannitol was added on reaching the end-point of "Sofnol No. 1."

Curves I and II (Fig. 1) represent, respectively, the titration when a given sample of fruit is incompletely and completely charred. In Expt. 1, the large volume of sodium hydroxide required to change the *p*H value from 4·4 to 6·0 accounts for the much greater effect of incomplete charring when methyl orange was used. Curve III represents the titration of the extract from an incompletely charred mixture of sugars. It is similar to Curve I, and suggests that the buffer action may well be due to acids produced during the partial charring of sugars in the fruit. There is a point of inflexion of Curve III at *p*H 3·7 corresponding to a

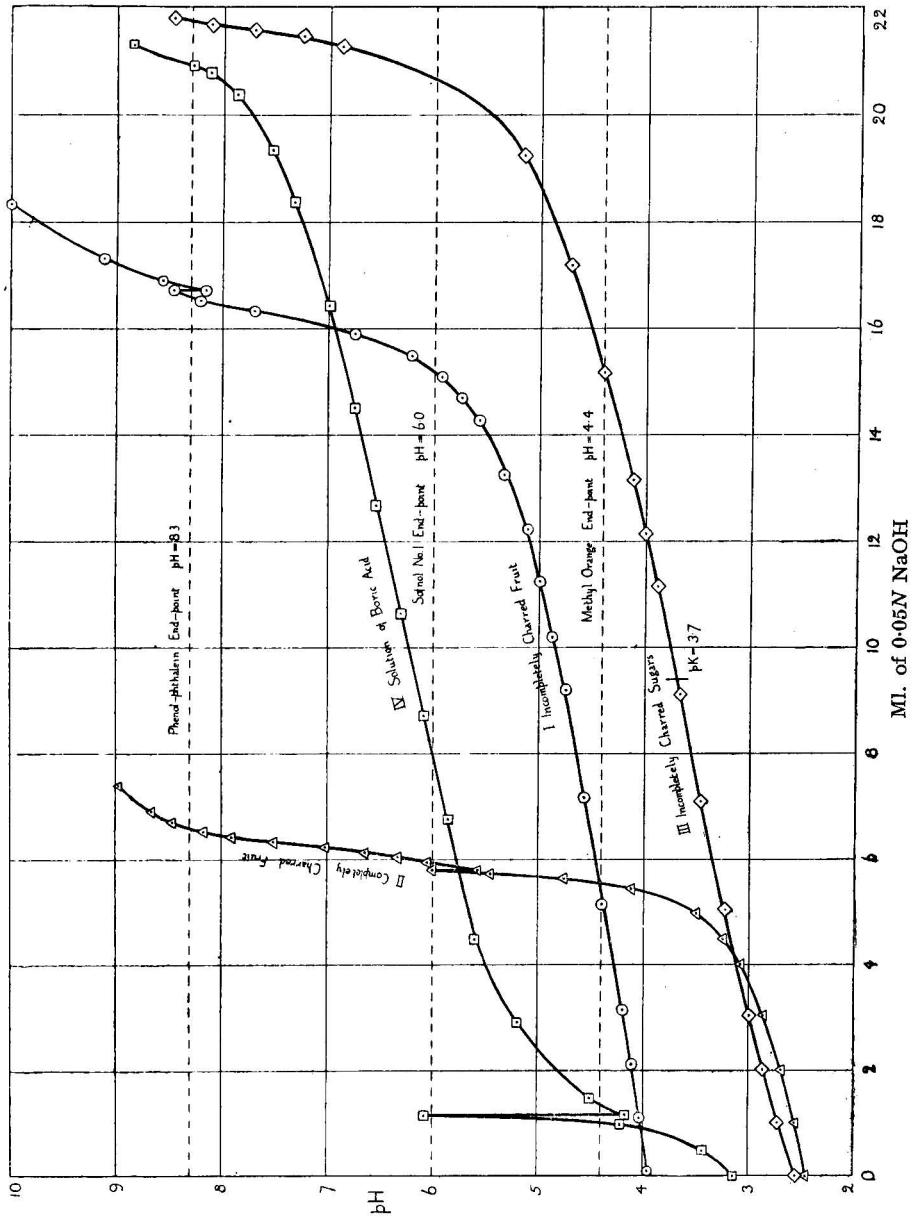
pH
Ml. of 0·05N NaOH
Phenol-phthalein End-point pH=8·3
Solution of Boric Acid
Satrol Nal End-point pH=6·0
I Incompletely Charred Fruit
Methyl Orange End-point pH=4·4
II Completely Charred Fruit
III Incompletely Charred Sugars
pK=3·7

FIG. 1.

TABLE V

Expt.	Description of solution titrated	Preliminary charring	*p*H from which titration was measured	Volume of 0·05 *N* NaOH ml.	H_3BO_3 equivalent to titration mg.	H_3BO_3 in the fruit p.p.m.
1	2/5 of extract from 25 g. South African raisins	Incomplete	4·4	11·19	34·6	3460
			6·0	1·43	4·4	440
2	4/5 of extract from 25 g. South African raisins	Complete	4·4	0·84	2·6	130
			6·0	0·72	2·2	110
3	Extract from 10 g. of sugars	Incomplete	4·4	6·36	19·7	—
			6·0	0·98	3·0	—
4	Solution containing 61·2 mg. H_3BO_3	—	4·4	19·78	61·1	—
			6·0	19·70	60·9	—

dissociation constant of the acidic substance equal to 2×10^{-4}. This therefore is a weak acid of the type of glycollic acid, the constant of which is $1{\cdot}5 \times 10^{-4}$. Curve IV shows that methyl orange and "Sofnol No. 1" give results in good agreement when a solution containing pure boric acid is titrated. The small difference of 20 p.p.m. between the results with the two indicators, which occurs in Expt. 2, was to be expected in view of the difficulty experienced in obtaining a complete blank with sugar (Table III).

GRAVIMETRIC DETERMINATION.—The volumetric method finally adopted was checked by determinations, by the Rosenbladt–Gooch method,[5] of the boric acid extracted in the usual way from 100 g. of fruit. Removal of phosphates greatly reduced the solid residue in the distilling vessel, but the recovery of boric acid was not affected. The results are shown in Table VI.

TABLE VI

Expt.	Description and treatment of extract	Weight of B_2O_3 mg.	H_3BO_3 found p.p.m.
1	From 100 g. of fruit; phosphates removed; ¾ of extract distilled	5·8	140
2	From 100 g. of fruit; phosphates removed; ¾ of extract distilled	6·8	160
3	From 100 g. of fruit; phosphates not removed; whole extract distilled	9·0	160
4	From 100 g. of fruit with 200 p.p.m. H_3BO_3 added; phosphates not removed; whole extract distilled	20·2	360
5	From 25 g. of fruit; determination by the volumetric method	—	150

Expts. 1, 2 and 3, which were made on a sample of Australian sultanas, show the order of reproducibility attained. The mean value agrees well with a result of 150 p.p.m. obtained volumetrically (Expt. 5). Expt. 4 is a determination on the same sample with boric acid added in the proportion of 200 p.p.m. It gave a result of 360 — 150 = 210 p.p.m. for the added boric acid. The agreement between the volumetric and gravimetric determinations is shown also in Table IV. Since the weight of boron trioxide obtained from 100 g. of fruit is only 6 to 9 mg., the errors inherent in the gravimetric method amount to about 10 per cent. This

accuracy is sufficient to show that the results obtained by the volumetric method, properly employed, are substantially correct.

The Boric Acid Content of Fruit from Various Sources

Procedure for the Quantitative Determination.—Twenty-five g. of minced fruit are weighed into a porcelain basin, moistened with 10 ml. of 2 *N* sodium hydroxide solution, evaporated on the steam-bath and charred. The mass is crushed in a glass mortar, returned to the basin and heated further. After cooling, the char is acidified with 2 *N* hydrochloric acid, 10 to 15 ml. of hot water are added, and the basin is warmed on the steam-bath to expel the bulk of the carbon dioxide. The contents of the basin are filtered into a 100-ml. calibrated flask, and the char is washed with hot water until the volume of the filtrate is about 50 ml. The filter and residue are returned to the basin, made alkaline with lime water (about 20 ml.), evaporated on the steam-bath and ignited to a white ash. This is dissolved in 2 to 3 ml. of 2 *N* hydrochloric acid, the solution is warmed for a few minutes and filtered, and the basin is rinsed into the 100-ml. flask. One ml. of 10 per cent. calcium chloride solution ($CaCl_2.6H_2O$) and 0·2 ml. of 1 per cent. phenolphthalein solution are added, followed by *N* sodium hydroxide, drop by drop, until the solution is faintly pink. Alkali (0·1 ml.) is added in excess, and the solution is diluted to the mark, well shaken, and filtered through a dry paper. To 75 ml. of the filtrate, placed in a 250-ml. conical flask, is added 0·1 ml. of a solution of "Sofnol No. 1" containing 1·2 g. in 1 litre of alcohol. The solution is acidified with *N* sulphuric acid until the red colour of this indicator is reached, boiled for 1 minute, cooled, and treated with a further 0·2 ml. of phenolphthalein. Sodium hydroxide solution (0·05 *N*) is used for the titration. When the "Sofnol No. 1" end-point is reached the reading is taken, 1 g. of neutral mannitol is added, and the titration is continued to the phenolphthalein end-point, which is taken arbitrarily as a pink colour lasting for half-a-minute. An allowance is made for the titration in a blank experiment. This is about 0·1 ml. No further addition of mannitol should be made unless the amount of boric acid is much greater than is normally found in dried fruit. One ml. of 0·05 *N* sodium hydroxide is equivalent to 3·09 mg. of boric acid, H_3BO_3.

Discussion of Results.—The results of 41 determinations are summarised in Table VII. Results obtained by Scott Dodd[3] are also given. Where comparison is possible the difference between the two sets is generally less than 40 p.p.m. When a number of determinations have been made upon one type of fruit from a particular source, Scott Dodd's results lie within the range found. The maximum value found for the boric acid content is 250 p.p.m., and the minimum 100 p.p.m. The results on 10 samples of Australian currants, known to have been untreated, vary between 130 and 180 p.p.m. Of other types of fruit, 7 may be assumed to have been untreated, and give results from 100 p.p.m. to 250 p.p.m., which is the maximum variation shown by any of the samples untreated or treated. That this proportion of boric acid is present as a natural constituent in all vine products is confirmed by the determination on English hot-house grapes, which have a boric acid content of 170 p.p.m., calculated on the dried fruit. Examination of the results obtained on samples of fruit known to

have been treated in a variety of ways, fails to show that any particular treatment has an appreciable effect on the boric acid content. In order thoroughly to investigate this point, the boric acid present in a given sample of fruit must be determined before and after treatment, and this has not been possible. The effect of any of the methods of treatment in regular use can only be slight, and the boric acid content will tend to be diminished, *e.g.* by extraction in the alkaline dips. The deliberate addition of boron compounds to the fruit is highly improbable, since no useful purpose would be served. This is emphasised by Scott Dodd in an addendum to his paper.[3] It is evident that a boric acid content greater than 250 p.p.m. is very unusual. A single result of 1000 or 2000 p.p.m. should be regarded with extreme suspicion if methyl orange has been used as preliminary indicator, since it may readily be due to incomplete charring.

TABLE VII

Place of origin	Type of fruit	No. of samples analysed	H_3BO_3 found			Results by Scott Dodd
			Max. p.p.m.	Min. p.p.m.	Mean p.p.m.	
Australia	Sultanas	10	250	130	180	220
,,	Currants	14	200	130	160	130
,,	Raisins	2	250	170	210	—
,,	Muscatels	2	200	200	200	—
,,	Lexias	1	—	—	150	—
South Africa	Sultanas	1	—	—	130	—
,,	Raisins	1	—	—	110	—
California	Sultanas	3	150	120	130	—
,,	Raisins	—	—	—	—	130
Greece	Currants	2	200	100	150	100, 140
,,	Sultanas	1	—	—	170	—
Crete	Sultanas	1	—	—	100	—
Smyrna	Sultanas	1	—	—	220	120, 180
Spain	Raisins	1	—	—	100	—
,,	Muscatels	—	—	—	—	150, 120
England	Grapes (dried)	1	—	—	170	—

I wish to thank Messrs. R. H. Purdie and R. C. Terry for placing at my disposal most of the results recorded in Table VII; also the Australian Dried Fruits Board, and in particular Mr. J. J. S. Scouler for facilitating the investigation.

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BIOLOGICAL FIELD STATION
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
SLOUGH, BUCKS.

Studies in Internal Electrolysis, I

THE DETERMINATION OF SMALL QUANTITIES OF CADMIUM AND NICKEL IN ZINC

By JAMES G. FIFE, B.Sc., A.I.C.

Determination of Cadmium.—The determination of cadmium in zinc by the method of "internal electrolysis" has been described by Collin,[1] who used a sulphate solution.

It has, however, been found by several workers in this laboratory that the method sometimes gives unreliable results, and the object of the present investigation was to ascertain, if possible, the cause of the unreliability and to provide a method of eliminating all factors leading to uncertain results.

The apparatus employed was substantially the same as that used by Collin and described by Sand.[2] A few minor modifications were made as follows:

(*a*) Instead of the stand used by Collin the electrolytic stand described by Sand[3] was used.

(*b*) The lid employed was made in one piece and had a central hole for holding the glass guide-tube of the stirrer, and two holes of 2-cm. diameter each 2·5 cm. distant from the centre, for the anodes. A further hole was drilled, having its centre 2·5 cm. distant from the centre of the lid, and of 2-cm. diameter, which was wide enough to allow the introduction and removal of the stem and tab of the cathode.

(*c*) The glass rods which serve to hold the cathode in position were found to be easily broken, and were replaced by a piece of wide glass tubing retained in position by a cork annulus disposed around the guide-tube for the stirrer.

(*d*) The anodes, which were made of zinc strip, were not provided with tabs, but slots were cut in their ends, so that they could be attached directly to the cathode by means of the terminals provided on the stand.

(*e*) The parchment thimbles were secured to the anodes by rubber bands instead of threads.

In order to investigate Collin's method, the anodes and cathode were not short-circuited but were connected with the terminals of a shunted unipivot micro-ammeter. The latter was also capable of measuring the voltage on open circuit by a simple switching arrangement.

A determination was carried out by the method described by Collin, and the current was observed meanwhile. After 20 minutes (*i.e.* a somewhat longer time than that recommended by Collin) the electrolysis was interrupted and the deposit weighed. It was found that of the 4 mg. introduced, 2·3 mg. had been deposited. The deposition was continued and after 82 minutes the current became constant, and on re-weighing the cathode it was found that the whole of the cadmium had been deposited.

A further experiment was made in which electrolysis was continued until the current became constant, whereupon a quantity of cadmium solution equal to

that first introduced was added, and it was found that the current only rose to about one-third of the initial value.

This experiment, together with the observation of white deposits on the anodes, led to the conclusion that the unreliable results obtained by the method were probably due to the deposition of basic zinc salts on the anodes which set up transfer resistances.

Experiments were therefore made to overcome the difficulty introduced by transfer resistances, and it was found that this could be achieved by the use of a chloride solution (zinc chloride and ammonium chloride) in both the anode and cathode compartments. Care should be taken, however, not to have the concentration of ammonium chloride too high, since it was found that the use of a solution containing 20 per cent. of ammonium chloride led to low results, presumably owing to complex-formation.

The use of an anolyte consisting of an aqueous solution containing zinc chloride equivalent to 5 g. of zinc and 10 g. of ammonium chloride per 100 ml., and of a catholyte consisting of approximately 300 ml. of solution containing the cadmium to be determined, zinc chloride equivalent to 5 g. of zinc, 30 g. of ammonium chloride, 5 ml. of 5 per cent. sodium acetate solution, 2 drops of 2 per cent. hydrochloric acid and 0·5 ml. of 50 per cent. hydrazine hydrate solution was found to give satisfactory results as shown in Table I.

TABLE I

No. of expt.	Cadmium added g.	Cadmium found g.	Time of electrolysis Minutes
1	0·0016	0·0015	18
2	0·0032	0·0033	20
3	0·0048	0·0047	34
4	0·0032	0·0030	24
5	0·0069	0·0070	45
6	0·0086	0·0085	30
7	0·0172	0·0171	35
8	0·0344	0·0336	45
9	0·0344	0·0358	110
10	0·0344	0·0356	82
11	0·0258	0·0258	44
12	0·0344	0·0351	66
13	0·0344	0·0344	75
14	0·0043	0·0043	30
15	0·0043	0·0041	25
16	0·0060	0·0059	37

In Expt. 4, 10 g. of sodium sulphate ($Na_2SO_4.10H_2O$) was also added to the catholyte, and it is evident that the presence of SO_4 ions in the catholyte does not interfere with the determination.

Furthermore, in Expts. 11 and 12, 1 g. of hydroxylamine hydrochloride was used instead of the hydrazine hydrate, and in Expts. 13 to 16, 1 g. of hydrazine hydrochloride was used instead of the hydrazine hydrate, and 5 ml. of 5 per cent. acetic acid were substituted for the hydrochloric acid.

In some of the experiments recorded in Table I the cadmium was added in two equal portions, and it was found that, on the addition of the second portion, the current rose to approximately the value observed after adding the first portion, thus proving that in this instance no badly conducting layer had been formed. Visual examination likewise disclosed no deposit but only slight corrosion.

A further series of experiments was made, in which a slightly different catholyte and the same anolyte as described above were used. The catholyte consisted of an aqueous solution of about 300 ml. containing the cadmium to be determined, zinc chloride equivalent to 5 g. of zinc, 30 g. of ammonium chloride, 2 g. of sodium acetate, 1 g. of hydrazine hydrochloride and 5 ml. of 5 per cent. acetic acid. A period of 30 minutes is recommended for amounts of cadmium less than 10 mg. and 45 minutes for larger quantities of cadmium. The cadmium was added in the form of a solution of cadmium chloride containing cadmium equivalent to 0·162 mg. per ml. in expts. 1 to 5, and 1·72 mg. per ml. in expts. 6 to 23.

The results obtained with this catholyte, which is to be recommended, are shown in Table II.

TABLE II

No. of expt.	Cadmium taken g.	Cadmium found g.	Time of electrolysis Minutes
17	0·0017	0·0017	30
18	0·0034	0·0034	30
19	0·0052	0·0051	30
20	0·0086	0·0085	30
21	0·0129	0·0128	45
22	0·0172	0·0171	45
23	0·0344	0·0348	45

In all these experiments the temperature of electrolysis was approximately 70° C., and the pH of the catholyte in all the experiments recorded in Tables I and II was about 4·5.

DETERMINATION OF SMALL QUANTITIES OF NICKEL IN LARGE QUANTITIES OF ZINC.—Hollard and Bertiaux[4,5] have described a method for the determination of nickel in zinc, the nickel and zinc being present as sulphates, in which an excess of ammonia together with ammonium sulphate and magnesium sulphate was used. Besides the defects of the apparatus referred to by Sand[2] the method has the defect that several hours are required to carry out a determination, and a temperature of 95° C. is employed, which will undoubtedly result in the loss of ammonia unless special precautions are taken.

I have found that nickel, in the presence of a large excess of zinc can be rapidly determined in a trustworthy manner by means of the apparatus used in the determination of cadmium described above.

The anolyte employed consisted of an aqueous solution containing zinc chloride equivalent to 5 g. of zinc, 10 g. of ammonium chloride and 17 ml. of ammonium hydroxide (sp.gr. 0·880) per 100 ml. The catholyte, consisting of approximately 300 ml. of solution, contained the nickel to be determined, zinc chloride equivalent to 5 g. of zinc, 30 g. of ammonium chloride and 2 g. of sodium

sulphite ($Na_2SO_3.7H_2O$). The nickel was added as a solution of nickel chloride containing nickel equivalent to 1 mg. per ml. The electrolysis was carried out at approximately 65° C. The results are given in Table III.

TABLE III

No. of expt.	Nickel added g.	Nickel found g.	Time of electrolysis Minutes
35	0·0035	0·0035	43
36	0·0035	0·0035	30
37	0·0069	0·0072	37
38	0·0115	0·0112	58
39	0·0115	0·0120	43
40	0·0163	0·0163	44
41	0·0163	0·0163	46
42	0·0230	0·0227	45
43	0·0345	0·0337	45
44	0·0012	0·0011	30
45	0·0046	0·0046	45
46	0·0092	0·0091	40
47	0·0138	0·0139	45

Expts. Nos. 41, 44 and 45 were carried on until constant weight was obtained, thus proving that a prolongation of the experiment has no harmful effect.

It should be noted that a large excess of ammonia should be used and that temperatures above 70° C. should be avoided, since otherwise incorrect results may be obtained, probably owing to loss of ammonia.

The use of a sulphite, recommended by Hollard[6] and verified by Lassieur,[7] was found to be advantageous.

I wish to thank Dr. Sand for his interest in this work.

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

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.

POISONING BY SODIUM NITRITE

RECORDED cases of poisoning by sodium nitrite are so rare that it is perhaps as well to record the following fatal cases which recently occurred at Middlesbrough, as the result of mistaking sodium nitrite for common salt.

On Sunday, May 31st, 1936, a man, aged 44 years, his wife, aged 42 years, and a daughter of the wife by a former husband, aged 5 years, collapsed and died shortly after eating their dinner.

So far as could be ascertained, the man and woman died approximately within an hour after partaking of the meal. The child was removed to the local infirmary and its stomach washed out, but it died after an illness of about 3 hours. The symptoms observed previous to death were characteristic of this type of poisoning, namely, difficulty in breathing, marked cyanosis, vomiting, and finally stupor and collapse.

The dinner consisted of meat, potatoes, cabbage, Yorkshire pudding, rhubarb tart and custard. A salt-cellar on the table contained an upper layer of a salt of a faint yellow colour and a lower layer of white salt similar in appearance to prepared table salt.

A basin was subsequently found containing about 4 ounces of salt similar in appearance to that of the upper layer in the salt-cellar. The contents of the basin and the upper layer in the salt-cellar were found to be sodium nitrite of commercial purity containing 98 per cent. of the pure salt.

The composition of the lower layer in the salt-cellar corresponded with that of prepared table salt containing 98·2 per cent. of sodium chloride.

The following amounts of nitrites (as sodium nitrite) were found in the organs, etc., received for examination:

	Sodium nitrite g.
Man's stomach	4·275
Woman's stomach	1·284
Child's stomach (washed out previous to death) ..	0·005
Child's vomit	1·047

The unconsumed portions of the foodstuffs forming the meal contained the following percentages of nitrites (as sodium nitrite).

	Sodium nitrite Per Cent.
Yorkshire pudding	4·50
Potatoes	0·75
Cabbage	6·50
Joint of meat (outer layer)	0·15
Joint of meat (interior)	0·015
Rhubarb tart	Nil
Custard	0·015

It was impossible to form a definite idea of the quantity of sodium nitrite taken by any of the three persons, as, unfortunately, neither the vomit of the man nor of the woman, nor the contents of the child's stomach previous to washing

out were retained for examination, but the quantity must have been appreciably in excess of the amounts subsequently recovered from the organs, etc.

No definite evidence could be obtained as to the origin of the sodium nitrite, but the man was employed at the Billingham Factory of the Imperial Chemical Industries, Ltd., and had access to the sodium nitrite plant at those works.

A sample of the sodium nitrite found in the house was examined by Mr. W. C. Hughes—chief analyst at the factory referred to—who stated that its composition was similar to that of the product made by his firm, and that was as far as it was possible to go in the matter.

The method used for the determination of the nitrite-content of the specimens examined was extraction with water, precipitation of the proteins with basic lead acetate, addition of potassium iodide, and titration of the liberated iodine with sodium thiosulphate in an atmosphere of carbon dioxide; the Griess alpha-naphthylamine and sulphanilic acid colorimetric method was also used. A. SCHOLES

Note.—A case of poisoning by nitrite is recorded in THE ANALYST, 1936, 614.—EDITOR.

THE DETECTION OF NITRITES

A REAGENT consisting of dimethylaniline and sulphanilic acid in equi-molecular proportions has been found useful for the detection of nitrites. It is prepared by dissolving 1 g. of dimethylaniline and 1·5 g. of sulphanilic acid in 100 ml. of $N/2$ hydrochloric acid.

In applying the test 2 drops of the reagent are added to about 10 ml. of the solution under examination; in the presence of a nitrite a red colour is produced. Alternatively, the test can be carried out with one drop of the solution on a filter-paper.

Very dilute solutions should be left to stand for ten minutes to allow the colour to develop, and it is advisable to use rather more of the reagent (1 ml.). A solution containing 0·05 mg. of NO_2 in 50 ml. (1 in 1,000,000) will develop a colour in 10 minutes, which is perceptible if the tube is compared with a similar tube containing no nitrite.

The colour is due to the formation of methyl orange, which is turned red by the acid present. The sulphanilic acid is diazotised by the nitrite, and the product immediately couples with the dimethylaniline.

With more concentrated solutions (exceeding 1 in 100,000) a yellow colour is first produced, and this, on standing, changes to orange and ultimately to red. This appears to be due to the interaction of nitrous acid and dimethylaniline, with the formation of a yellow nitroso-compound, *p*-nitroso-dimethylaniline. It should be noted, however, that the mixture of dimethylaniline with sulphanilic acid is much more sensitive than dimethylaniline alone, the limits being approximately 1 in 1,000,000 and 1 in 100,000, respectively.

The formation of a yellow colour in more concentrated solutions can be avoided by adding the two reagents separately. If sulphanilic acid alone is first added, followed after a short interval by a solution of dimethylaniline in $N/2$ hydrochloric acid, a pink colour is produced.

The test can be applied colorimetrically in Nessler glasses for the determination of the approximate concentration of very dilute solutions of nitrites—ranging from 1 in 1,000,000 to 1 in 100,000. As, however, the intensity of colour depends upon time as well as upon concentration, it is essential that the standard colours should be produced as nearly as possible simultaneously with that in the solution under examination.

J. C. GIBLIN
G. CHAPMAN

PERRINS LABORATORIES
ROYAL GRAMMAR SCHOOL
WORCESTER

A RAPID METHOD OF SAPONIFICATION

THE method consists in replacing the ethyl alcohol in alcoholic potash solutions by ethylene glycol monoethyl ether. For the sake of brevity this compound is hereinafter termed "the solvent." The chief objects of this substitution are to raise the temperature of saponification (the solvent boils at 134° C.), to form a complete solution of sample in reagent and so to accelerate the reaction.

It has been found that the solvent is readily rectified by leaving it overnight on a little solid sodium hydroxide and then re-distilling. Potassium hydroxide is readily soluble in the solvent—perhaps more so than in ethyl alcohol—and a pale solution results. This solution becomes very little discoloured when kept.

Using an $N/2$ solution I have found that when fatty matter is boiled therewith saponification is almost instantaneous. Even with compounded mineral oils, wool-fat and carnauba wax saponification is complete within 15 minutes, and the titration end-point is exceedingly sharp. Not all compounded oils go into complete solution in the reagent, but the saponification is nevertheless complete within 15 minutes.

The results obtained with pure fatty oils are identical with those obtained with alcoholic potash as the reagent.

Objection may be made to the cost of the solvent (14s. per gallon). Having regard to the small quantity used in a single test, however, this cannot be considered excessive.

W. R. STEET

18, CLIFTON ROAD
LONDON, N.8

AN AGAR AND POTASSIUM CHLORIDE BRIDGE FOR USE WITH CALOMEL HALF-CELLS

FOR the measurement of *p*H of soil samples it is convenient to employ the saturated calomel-saturated quinhydrone cell with an agar and potassium chloride bridge. This system gives a relatively high current; it is quick, and, except in special cases (*cf. Trans. Third Int. Congress Soil Sci.*, 1935, **1**, 127), accurate. Note may be made, however, of several points which have been found to give a more efficient and speedy procedure. The ordinary inverted-U type of agar and potassium chloride bridge is unsuitable for soil work, since potential drift, due to base-exchange phenomena, may set in if a wide-bore tube is used; after a few measurements the end of the bridge becomes contaminated with soil particles; if a pressure increase should take place within the cell (as, for example, through a rise of temperature, or even in setting up the electrode) the agar and potassium chloride gel is forced over and breaks off at the free end of the bridge.

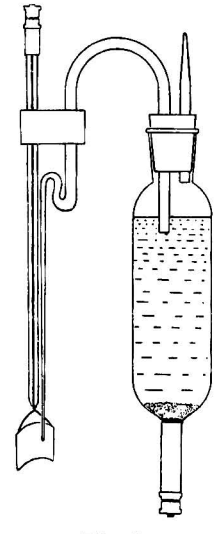

Fig. 1.

To eliminate these difficulties, a bridge (see Fig. 1), formed from a tube drawn to a fine capillary and bent at the top of the latter to form an S, was devised. It is filled by immersing the wide end in agar and potassium chloride gel, and applying suction to the capillary. The S-bend is sufficient to prevent the gel from syphoning out of the bridge, and small portions of the capillary can be broken off from time to time to expose a fresh surface. The bridge is usually attached to the cell through a rubber stopper, which also carries a small piece of glass tubing drawn out to a capillary. This remains open until the stopper and bridge are firmly fixed in position, after which it is sealed off to prevent

"creeping" of the potassium chloride. In this way the bridge can be attached without exerting pressure on the agar gel.

The platinum electrode is a piece of foil, $\frac{1}{2}$ in. $\times$ $\frac{1}{2}$ in., bent to form a semi-circle, and attached by platinum wire to a glass tube. The electrode is mounted on a two-holed rubber stopper, which is cut vertically so that it can be slipped round the bridge. In this way both the half-cells can be held in one clamp and raised and lowered together into the medium under test; in addition, washing is greatly facilitated.

This system has been in use for over five years, and has given every satisfaction. It has also been found convenient to use it with a glass electrode, in which case the platinum electrode is removed from the split stopper and a glass electrode substituted. If oxidation-reduction potential is also to be measured, a three-holed split rubber stopper is used, on which is mounted the glass electrode and the unplatinised platinum electrode. By connecting the appropriate leads with the potentiometer both pH and rH may be measured without removing the electrodes from the medium under examination.

IAN M. ROBERTSON

MACAULAY INSTITUTE FOR SOIL RESEARCH
CRAIGIEBUCKLER, ABERDEEN

THE DETERMINATION OF SMALL AMOUNTS OF COPPER IN TIN, BY CONTROLLED POTENTIAL

A METHOD for the determination of traces of copper in tin is of industrial importance for such purposes as ascertaining impurities in commercial tin, observation of the penetration of copper into the tin layers of tinned-copper products, etc.

Electrolytic methods for the separation of metals by controlled potential, using rotating electrodes, were first worked out by Sand,[1] and the first satisfactory method for the separation of tin and copper, by the use of controlled potential, was described by Schoch and Brown,[2] and later confirmed and improved by Lassieur[3] and by Lindsey and Sand.[4] This method, based on the separation in a chloride solution, does not work when the proportion of copper to tin is extremely small. This difficulty has previously been noted by Fischer,[5] and possibly explains the fluctuations in current noted by Lassieur and by Lindsey and Sand. Lassieur has also described a method for the electrolytic determination of traces of copper in tin.[6] In this method, the tin is first precipitated as the insoluble oxide, and the copper determined in the solution. This would tend to give low results, as some of the copper would be retained in the tin precipitate. By the following method, however, consistently satisfactory results are obtained, even with extremely small amounts of copper.

Ten g. of tin are dissolved with the aid of heat in a mixture of 100 ml. of conc. hydrochloric acid and 15 ml. of conc. nitric acid. After solution, the excess of chlorine is boiled off, the flask is cooled, and 30 ml. of conc. sulphuric acid are cautiously added; the whole is evaporated by boiling until fumes have appeared and the mixture is distinctly turbid, owing to the separation of stannic sulphate. The mixture is allowed to cool somewhat and is then diluted with 50 ml. of water, boiled to dissolve the stannic sulphate, and cooled. This should give a yellow solution, entirely free from chloride ions. As traces of lead (originally present in the tin) produce lead sulphate, any insoluble matter is filtered off on a Gooch crucible and washed with a little $N/2$ sulphuric acid. The filtrate is diluted to about 150 ml., 10 ml. of a 2 per cent. solution of hydrazine sulphate are added, and the solution is electrolysed with the use of the anode and cathode and saturated calomel electrode of the type used by Lindsey and Sand.[4] The auxiliary electrode contains the system ($Hg \mid HgCl_2 \mid KCl$(satd.) $\mid N Na_2SO_4$).

Electrolysis is commenced with an auxiliary electrode-to-cathode potential of 0·2 volt at room temperature; this gives a current of 0·05 amp. After two or three minutes, the auxiliary potential is raised to, and maintained at 0·4 volt. The current rises to about 0·3 amp. and falls eventually to about 0·15 amp. After 20 minutes the liquid in the tip of the auxiliary electrode is flushed out, and the electrolysis is continued for a further 10 minutes.

In experiments in which pure tin was used and the requisite amounts of copper were added as copper sulphate after solution, the following results were obtained:

Copper taken (mg.)	0·0	3·0	3·0	4·0	5·0	5·0	5·0	5·0	12·5
Copper found (mg.)	0·0	3·0	3·0	3·9	4·9	4·8	5·0	5·0	12·6

I wish to thank Dr. Sand for his suggestions and interest in this work.

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SYDNEY TORRANCE

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

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.

CITY OF LONDON

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1935

THE work of the Public Analyst (Mr. A. J. C. Lickorish, F.I.C.) is summarised in the section of the Medical Officer's Report dealing with the supervision of food and drugs. Of the 1032 samples submitted, 771 were bought informally. Sixteen of the informal, and 11 of the formal samples were reported against, including 6 of 221 samples of milk.

TIN IN CANNED GOODS.—Seven of 48 samples of canned goods were found to contain tin in excess of 2 grains per lb., namely, canned spinach, 3·04 and 4·75; canned celery, 3·35; canned haricots verts, 2·21; canned apricots, 4·9; canned sild, 3·4 and 3·2 grains per lb. Five of the canned vegetable products were procured from one vendor, who surrendered five bushels of unsold stock for destruction. The importers of the canned fish were communicated with, and they immediately instituted enquiries to remedy the matter.

SMOKE AND ATMOSPHERIC POLLUTION.—A rain gauge is mounted upon the roof of one of the Corporation's buildings in Golden Lane, and the rain-water from a known area of surface is collected monthly and submitted to the Public Analyst.

The results for six of the months, calculated into metric tons per square

kilometre, were as follows; the figures for the Meteorological Office, South Kensington, and for Victoria Park are added for comparison:

Month of the Year 1935	Place	Rainfall mm.	Metric tons per square kilometre: Insoluble matter: Tar	Insoluble matter: Carbonaceous other than tar	Insoluble matter: Ash	Soluble matter: Loss on ignition	Soluble matter: Ash	Total solids	Included in soluble matter: Sulphates (SO_3)	Included in soluble matter: Chlorine (Cl)	Included in soluble matter: Ammonia (NH_3)
Jan.	Meteorological Office	24·3	0·33	5·45	7·43	1·31	2·44	16·96	1·09	0·73	0·08
	Golden Lane ..	—	0·56	5·67	7·76	36·86	48·25	99·103	27·65	8·61	0·85
	Victoria Park ..	26·5	0·06	0·91	1·51	0·69	1·70	4·87	0·69	0·31	0·035
Mar.	Meteorological Office	7·6	0·16	1·50	2·20	0·76	1·72	6·34	0·52	0·44	0·008
	Golden Lane ..	11·705	0·12	1·96	0·78	1·62	4·49	8·978	0·92	0·65	0·06
	Victoria Park ..	7·8	0·09	1·43	1·41	0·44	1·03	4·40	0·48	0·20	0·04
May	Meteorological Office	33·2	0·18	2·19	3·12	1·06	2·06	8·61	0·68	0·37	0·01
	Golden Lane* ..	18·452	0·21	0·83	0·77	1·23	2·19	5·22	0·57	0·35	0·04
	Victoria Park ..	33·3	0·05	0·92	1·69	0·40	1·46	4·52	0·60	0·27	0·05
July	Meteorological Office	13·3	0·09	0·87	1·46	0·80	1·73	4·95	0·50	0·20	0·027
	Golden Lane ..	12·118	0·16	0·03	0·11	0·73	0·89	1·928	0·30	0·22	0·03
	Victoria Park ..	15·3	0·01	0·12	0·37	0·15	0·95	1·60	0·39	0·08	0·03
Sept.	Meteorological Office	77·8	0·11	0·50	0·59	2·18	3·26	6·64	1·28	0·72	0·02
	Golden Lane ..	61·965	0·25	1·47	2·82	2·11	1·98	8·634	1·20	0·80	0·01
	Victoria Park ..	50·7	0·11	1·70	3·08	0·61	2·53	7·98	1·08	0·40	0·11
Dec.	Meteorological Office	67·1	0·29	4·14	8·24	0·81	2·68	16·16	1·11	0·61	0·011
	Golden Lane ..	61·965	0·34	1·25	4·19	3·34	3·72	12·847	1·57	1·06	0·21
	Victoria Park ..	52·3	0·10	2·06	3·35	1·05	2·09	8·65	1·15	0·39	0·06

* Bottle overflowed.

CITY OF LEICESTER

Annual Report of the City Analyst for the Year 1935

Bacteriological Purity of Shell-fish.—Six samples of mussels were examined by the bacteriological technique recommended by the Worshipful Company of Fishmongers; a minimum standard of 60 per cent. cleanliness is recommended if the fish are to be passed for human consumption. All the samples were condemned, and the public were warned by a local press notice to cook all mussels before eating. Four of 12 samples of oysters were condemned.

Declared Analyses of Patent Medicines.—To avoid payment of Government Stamp Duty on patent medicines it is now a common practice for pharmacists to publish the percentage composition of many drugs, together with a declaration that no proprietary rights are claimed. Examination of a number of such articles suggests that these declared analyses are sometimes a matter of form rather than a true indication of the composition of the medicine. Absolute accuracy, of course, is not expected, but about 10 per cent. variation from the amount declared should allow sufficient margin for commercial working.

One sample, sold as a "Fever and Cold Mixture," was declared to contain, *inter alia*, 12·5 per cent. of Syr. Tolu and 5·0 per cent. Sp. Aether Nit. No evidence of the latter ingredient was obtainable, and only one-third of the declared amount of syrup of tolu was present. Another sample contained 23·0 per cent. v/v of glycerin, whereas the declared formula indicated only 12·5 per cent. A third sample of 25 pills, each supposed to contain one drachm of ammoniated quinine, consisted of two kinds of pills, 10 of which were of the correct composition, whilst the other 15 were ordinary quinine pills devoid of ammonia. In such cases, when pre-packed

articles are at fault, the retail pharmacist is obviously the victim of circumstances rather than the culprit. It was therefore decided to call the attention of the local Pharmaceutical Union to the matter, and this body caused a notice to be inserted in the *Supplement*, issued to all members in the district, warning pharmacists to protect themselves by obtaining a guarantee from the packing house supplying each individual article.

FLOWERS OF SULPHUR.—One sample did not comply with the B.P. test for acidity. Free sulphuric acid develops in this article on storage and exposure to the air, and unless the free acid is considerably in excess of the B.P. limit it is fair to regard the irregularity as a technical infringement of the Regulations rather than a fraud likely to prejudice the purchaser. An interesting point noted was that this sample was distinctly deeper in colour than 5 other samples of lower acidity taken at the same time.

F. C. BULLOCK

The National Physical Laboratory

PHYSICAL CONSTANTS OF PURE METALS

NUMEROUS physical constants of pure metals have been determined during the past fifteen years at the National Physical Laboratory, Teddington. The results have now been collected, and are published in a pamphlet* in a convenient form for reference.

Part I of the pamphlet contains data for some specially pure metals which have been prepared in the course of researches at the Laboratory. The metals are iron, chromium, manganese, beryllium, cadmium, magnesium and tin, and tables are also included giving the surface tensions of liquid metals and the lattice parameters of various metals.

IRON.—For the preparation of pure iron, the crude iron prepared by either the electrolytic or the chemical process, and containing relatively large quantities of oxide of iron and traces of other impurities, was used. This material was melted under slightly oxidising conditions in porous crucibles of pure alumina. By this means the more readily oxidisable impurities were retained as oxides, which separated from the metal and were mainly absorbed by the porous material of the crucible. After cooling, the ingot was cleaned from adhering oxide and a thin layer of metal removed, by machining, from all surfaces. The iron was then re-melted, and a stream of purified hydrogen passed over the surface of the liquid metal in order to remove the remainder of the oxygen present. A further melting *in vacuo* was next undertaken to extract as far as possible any gas left in the iron after the hydrogen treatment.

The following physical constants, *inter alia*, were recorded:

Melting-point: 1527° ± 3° C., obtained by the optical pyrometer method (m.p. of palladium = 1555° ± 2° C.). The sample of iron contained 0·010 per cent. of carbon, 0·030 per cent. of silicon, 0·014 per cent. of phosphorus, 0·05 per cent. of oxygen, with traces of sulphur and manganese.

Density: 7·871 ± 0·002 g. per ml. at 19° C.

Thermal conductivity:

Mean temperature, °C.	0	25	50	75	100	125	150	175	200
Thermal conductivity, k (c.g.s. units) ..	$(0{\cdot}19_4)$	$(0{\cdot}18_9)$	$0{\cdot}18_5$	$0{\cdot}18_0$	$0{\cdot}17_6$	$0{\cdot}17_2$	$0{\cdot}16_7$	$(0{\cdot}16_2)$	$(0{\cdot}15_8)$

* *Physical Constants of Pure Metals*, July, 1936. H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 6d. net.

Coefficient of expansion:

Mean temperature, °C. ..	0	25	50	75	100	125	150	175
Coefficient of expansion, $\times 10^6$..	(10·4)	(10·8)	11·2	11·6	12·0	12·4	12·8	(13·2)

Values in brackets determined by extrapolation.

Electrical resistivity:

Temperature, °C.	0	50	100	150	200
Microhms per cm.^{3}	(8·8)	11·5	14·5	17·8	(21·5)

CHROMIUM.—The pure metal was obtained by electro-deposition and treated with hydrogen to remove oxygen. A typical analysis gave: Carbon, 0·004; insol. residue, chiefly Cr_2O_3, 0·01 to 0·03 per cent.; sulphur, iron, aluminium and lead not detectable in 10 g.

Melting-point, 1830° C.; *Brinell hardness* (2 mm. ball, 40 kg. load), 108; *Electrical resistivity* (microhms per cm.^{3}, 13·1.

MANGANESE.—The metal was distilled *in vacuo*; total impurities less than 0·01 per cent.

Melting-point, 1242 ± 3° C.

BERYLLIUM.—The re-melted cathode metal contained 99·6–99·7 per cent. of beryllium (as metal), 0·1 per cent. of beryllium (as oxide), 0·2 per cent. of oxygen (as oxide), 0·05 per cent. of carbon, trace of silicon, 0·01 per cent. of iron, trace of aluminium, and 0·005 per cent. of nitrogen.

Melting-point, 1281° ± 2° C. *Density*, 1·82–1·84 g. per ml. *Reflectivity to white light*, 42 per cent. (Note.—This is the same as for stainless steel.) *Brinell hardness* (1 mm. ball, 10 kg. load), 100–120.

CADMIUM.—The data relate to cadmium of 99·98 per cent. purity.

Melting-point, 321° C. *Density*, 8·648 g. per ml. at 17° C. *Electrical resistivity* (microhms per cm.^{3}), at 20° C., extruded rod, 6·85; drawn wire, 7·59; at 100° C., extruded rod, 9·03; drawn wire, 9·94. *Tensile strength* (tons per sq. in.): Cast cadmium, 4·6; rolled cadmium, 1 day after rolling, 4·9; rolled cadmium, 100 days after rolling, 3·9.

MAGNESIUM.—Commercially pure magnesium was further purified by subliming the metal *in vacuo* at a temperature in the neighbourhood of 600° C. By subliming three times, the purity was raised from 99·93 per cent. to 99·97 per cent. A spectroscopic examination showed that, while the iron was greatly reduced in quantity by this treatment, the copper-content of the metal was not appreciably altered.

Melting-point, 659° ± 0·5° C.

TIN.—Measurements have been made of the viscosity of so-called "chemically pure" molten tin, by means of a method based upon the assumed correctness of the smoothed determinations of Sauerwald over a smaller temperature range than that of the present measurements. The results were as follows:

Temperature, °C.	240	300	400	500	600	700	800
Viscosity, poises	0·0191	0·0167	0·0138	0·0118	0·0105	0·00945	0·0087

The viscosity at the freezing-point (232° C.) obtained by extrapolation was 0·0195 poise. The small traces of foreign metals present in the tin used should not measurably influence the results.

Part II contains results obtained on metals of known high purity from outside sources. Data are given for melting-points, latent heats of fusion, specific heats, thermal conductivities, and coefficients of expansion. The results of measurements made in other institutions have, in many instances, been included, thus bringing together results which are later than those contained in the International Critical Tables.

Weights and Measures

REPORT BY THE BOARD OF TRADE FOR THE YEAR 1935*

THE Report deals with the proceedings and business of the Board under the Weights and Measures Act, and in accordance with past practice also deals with the work undertaken by the Standards Department under the Sale of Gas Acts, the Coinage Act, 1870, and the Petroleum (Consolidation) Act, 1928.

STANDARDS.—A new scheme for the re-verification of "first derivative" standards of the various legal denominations of weight and length has been agreed with the Metrology Department of the National Physical Laboratory, whereby the standards of mass will be re-verified triennially and standards of length quinquennially.

The vibration recorder (I.B. 3493) acquired during the year has been used to obtain permanent comparative records of the susceptibility of various weights and measures offices and gas-meter testing offices to vibrations.

The Stereometer (I.B. 3505).—This is an instrument designed in the Department for the determination of the density of weights without immersion. It is based upon a volume determination through the application of Boyle's law. Although it does not permit of so great accuracy, it saves standards from the harmful effects of immersion.

Disposal of Metre Bar.—The platinum-iridium bar acquired by the Department from the International Bureau of Weights and Measures in 1894 has been sold. Being an end-standard, *i.e.* one whose nominal length is defined by the distance between its end faces, it did not lend itself readily to inter-comparisons by ordinary means, and had proved to be of little service to the Department.

Other matters dealt with in the Report include the arrangements for the verification of local and working standards, the examination of patterns of weighing and measuring apparatus, the examination of candidates for certificates of qualification as inspectors, points arising out of the general administration of the Weights and Measures Act, and the verification of apparatus for testing the flashing-point of petroleum.

The fees received by the Department for the verification of standards of weight and measure and instruments, and for the examination of candidates amounted to £4366.

The contribution of Great Britain to the International Bureau of Weights and Measures for the year 1935 was equivalent to £692.

Various questions of general interest are summarised in an appendix giving replies to enquiries from local authorities and inspectors during the period.

Apothecaries' Measures.—A question was raised affecting the legality of an apothecary's conical measure which would not completely empty when tilted at an angle of 120°, as required by No. 31 of the Weights and Measures Regulations, 1907. It was represented that this requirement was unnecessary in respect of a measure which either was not to be used in the presence of the purchaser or, if so used, would usually be incomprehensible to him. The reply was sent that it was open to the local authority under No. 23 of the Regulations to apply for a dispensation from the requirement of No. 31 in this connection, but that before this step was taken it might be possible to persuade the maker of the measure to abandon conical-shaped measures in favour of cylindrical measures which were most satisfactory for the purpose in view. The maker subsequently agreed to adopt this course.

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1936. Price 6d. (postage extra).

Fruit and Vegetable Preservation Research Station, Campden

ANNUAL REPORT, 1934–1935*

In January, 1935, a conjoint meeting was held between representatives of the Ministry of Agriculture, the Food Investigation Board (Department of Scientific and Industrial Research), the University of Bristol and the Canning Industry. After a full discussion, all parties accepted a recommendation that, from October 1st, 1935, the responsibility for the administration of State grants in aid of the work of the Station should be transferred from the Ministry of Agriculture to the Department of Scientific and Industrial Research.

Under the new arrangement, however, contact with the Ministry of Agriculture will be maintained, and the Ministry will still be represented on the Management Committee. The connection with the University of Bristol still remains unchanged, and the Management Committee consists of seven representatives of the University, seven members nominated by the Canning Industry and three members appointed by the Department of Scientific and Industrial Research (one of whom will be a representative of the Ministry of Agriculture and Fisheries). It is also stipulated that all possible efforts must be made by those in charge of the Station to increase the amount of the contributions from the canning industry, with the dual object (*a*) of providing for the extension of the work and ensuring adequate prospects for the staff, and (*b*) of adjusting the proportion between the State grant and the subscriptions from the industry. The amount to be given each year will be determined in consultation with the University after consideration of the progress made in securing increased industrial support.

The present Report gives an account of the work of the Station during the year ended September 30th, 1935, other than the results of certain specific investigations published from time to time in a series of technical publications issued to subscribers.

National Mark Standards.—The National Mark Scheme for home-grown canned vegetables came into operation in June, 1930, and since that date samples collected at the factories and from retail shops have been officially examined at the Research Station. In 1933 a "score-card" system of assessment was introduced, and some valuable modifications were adopted in the following year. By this method of assessment a certain maximum number of points was allotted to each item—colour, texture, absence of defects, size grading, original weight of fruit or vegetable, density of syrup, etc.—the total maximum score being 100 points. Any sample falling below 85 points on the total, or below a "special minimum" which was allocated to each item, was considered to be below National Mark Standard. In addition, there was a "normal minimum" for each item which represented the score to be allotted where the full tolerance allowed in the regulations was made use of.

The Marketing Leaflet No. 20 of the Ministry of Agriculture and Fisheries (July, 1935) gives the standards and definitions of quality which have been gradually built up during the past few years.

Green Pea Varieties.—The results of eleven years' work on the suitability of the chief commercial varieties of peas for canning is summarised. The points discussed include cropping power, length and colour of haulm, size of pods, yield of peas from pods, colour and shape of peas, and susceptibility to frost and disease.

* Published by the University of Bristol, pp. 101. Introduction and Contributions by F. Hirst, M.Sc. (*Director*), and Contributions by W. B. Adam, M.A., A.I.C., G. Horner, M.Sc., N. B. McMaster, M.Sc., R. Hull, B.Sc., and G. S. Siddappa, M.A.

The problem of the classification of varieties of peas is discussed in Bull. No. 81, 1935, of the Ministry of Agriculture and Fisheries.

GASES IN CANNED FOODS.—The gas present in fresh vegetables is to a large extent removed by the blanching process which the vegetables receive before being canned. This is illustrated by the following results:

	Raw				Blanched			
		Composition				Composition		
Vegetable	Gas ml. per 100 g.	CO_2 Per Cent.	O_2 Per Cent.	N_2 Per Cent.	Gas ml. per 100 g.	CO_2 Per Cent.	O_2 Per Cent.	N_2 Per Cent.
Peas	18·0	60	6	34	2·7	31	1	68
Beans	12·8	42	4	54	2·0	17	13	71
Carrots	10·0	64	3	33	1·7	53	8	39
Peas (dried)	38·0	79	6	·15	1·2	22	10	68
Beans (dried)	13·0	56	7	37	1·2	31	6	63

Changes in Head-space Gases during Storage.—The proportion of carbon dioxide in the head-space in a normally filled can of vegetables varies between 11·5 and 14·0 per cent. The effect of storage is to reduce the oxygen-content. For example, the percentage of oxygen in the head-space in a can of whole carrots, fell from 6·6 on the first day to 0·3 after 7 days, and to 0·0 after 32 days.

Hydrogen in Canned Vegetables.—After long storage canned products of most types develop hydrogen, and the ends of the containers become blown. This is a common source of loss in canned fruits, but is only of occasional occurrence in canned vegetables. In the present series of experiments small quantities of hydrogen (0·5 to 1·5 per cent.) were found after about 15 weeks' storage, at normal temperatures. In blown cans, approximately three years old, the amounts of hydrogen in the head-space gases ranged from 31·7 to 78·8 per cent. All these cans were lacquered.

Unsound Cans.—The chief characteristic of the gases of cans which are spoiled by bacterial action is an abnormally high proportion of carbon dioxide. The following analyses show the percentage of carbon dioxide in the head-space gases of spoiled cans of vegetables:

	Head-gases (per cent.)			
Vegetable	CO_2	O_2	N_2	H_2
Peas	51	trace	49	nil
Peas	78	nil	22	nil
Beet	64	nil	33	3
Beet	42	nil	57	1
Beans	63	nil	37	nil
Beans	29	nil	71	nil

The head-space of sound cans normally contains more carbon dioxide and less oxygen than air. Hydrogen is rarely found in conjunction with abnormally high percentages of carbon dioxide; whenever found in the present investigations, its quantity was sufficiently small to be attributed to the ordinary process of corrosion. Gaseous hydrocarbons have so far not been found in the head-space of spoiled cans.

DETERMINATION OF COPPER IN TOMATO PURÉE.—It has been shown that imported tomato purée is liable to be contaminated with copper (*cf.* McLachlan, ANALYST, 1935, **60**, 753). Experiments have therefore been made to find the most suitable means of determining copper in this product, and the following method has been devised, in which the ashing procedure of McLachlan has been adopted:—Twenty to 30 g. of purée are dried in a silica dish on the water-bath and charred thoroughly over a naked flame, without allowing the material to be

ashed. The dish is cooled, and the carbonised mass is moistened with a few drops of water, treated with 15 ml. of sulphuric acid (25 per cent.), and crushed with a glass rod. The liquid is evaporated to about 8 ml., treated with 20 ml. of hot water, and filtered through a 9-cm. paper. The carbon particles in the dish are washed twice with 10-ml. portions of water, and then burned off at as low a temperature as possible (over-heating may result in loss of copper). The residual ash is moistened with water, the filtrate already obtained is added to it, and the liquid is evaporated to 8 ml., diluted with hot water, and filtered through the same paper, and the residue is washed as before. Finally, the filter-paper is dried and ignited in the dish at a low temperature, the filtrate is added, evaporated to 20 ml., and filtered through a fresh paper, and the dish and filter thoroughly washed.

The filtrate (about 60 ml.) is cooled, neutralised to methyl orange with 10 per cent. sodium hydroxide solution, then acidified with 4 ml. of 10 per cent. acetic acid, and treated with the following reagents: (i) 2 ml. of 10 per cent. ammonium thiocyanate solution; (ii) 2 ml. of saturated sodium pyrophosphate solution; (iii) 2 ml. of 20 per cent. (by vol.) pyridine solution. The liquid is mixed and shaken out with chloroform (5 ml., 3 ml. and 2 ml.). The third extract should be nearly colourless; if not, a further extraction is made. The united extracts are made up to 10 or 20 ml. and filtered through a dry paper, and 5 ml. of the filtrate are compared with standards made from pure copper sulphate, or the colour may be determined on the Lovibond scale, and the corresponding amount of copper read from a table or graph:

Copper, mg.	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8
Lovibond yellow units ..	1·1	2·4	3·6	4·7	5·8	6·9	8·0	9·1

The method is based on the formation of copper pyridine thiocyanate, as described by Biazzo (*Annali Chim. Appl.*, 1926, **16**, 96), and developed by Elvehjem and Lindow (*J. Biol. Chem.*, 1929, **81**, 435; ANALYST, 1929, **54**, 245). Ferric salts, if present, are rendered inert by the addition of the sodium pyrophosphate.

It is shown that the method gives accurate results with tomato purée in the presence of 2 to 8 mg. of ferric iron. For minute quantities of copper (0·005 to 0·01 mg.) the method of Sylvester and Lampitt (ANALYST, 1935, **60**, 376) is recommended.

"FLAT-SOUR" SPOILAGE IN CANNED PEAS.—It has been shown that the sugar (used as a constituent in making the brine or covering liquid) is the principal source of the thermophilic bacteria responsible for this type of spoilage. In this connection 16 samples of English, 2 of French and 6 of American sugars were examined. None of the English sugars was very heavily infected, but the foreign samples contained from 40 to 500 spores of thermophilic bacteria per 10 g. Obligate thermophiles were not among the strains isolated from samples of blancher-water or from 24 samples of sugars. The facultative thermophiles found are not capable of resisting such high temperatures as the obligate types, but they may, if introduced into the cans in large numbers, survive the heat treatment given in the sterilisation process, and, as they will grow at 37° C., they may cause spoilage under normal conditions of storage. Apart from using sugar relatively free from spores of thermophilic bacteria, the only other essential safeguard is thorough cleanliness in all parts of the plant.

SPOILAGE OF PROCESSED FRUIT BY *Byssochlamys fulva*.—This fungus is widely distributed in fruit orchards and plantations. To destroy the ascospores it is advisable to have a temperature of at least 190° F., and preferably 195° F., in the centre of the can during processing.

RIPENING OF GREEN PEAS.—Chemical analyses have been made of six varieties of peas commonly used for canning. The results showed that the round-seeded *Alaska* pea had a higher ratio of starch to sugar than the wrinkle-seeded varieties, and that the quality was relatively poor. The ripening process in all the varieties

showed two stages: (1) characterised by a fairly constant ratio of starch to sugar; the peas at this stage were all of high quality; (ii) a rapid stage, characterised by a sudden increase in starch and higher carbohydrates, and a decrease in sugar; there was a pronounced falling off in quality. The starch-content was much lower during a cool, than during a hot summer. At the "canning stage" there was a fairly characteristic ratio of peas to pods in all varieties, and the distribution of sizes was also fairly constant for each variety. The proportion by weight of peas to pods at this stage was about 27 to 29 per cent. for *Alaska* and *Gregory's Surprise*, and about 30 to 34 per cent. for *Lincoln, Thomas Laxton, Canners' Perfection* and *Charles the First.*

Cyprus

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1935

In his Annual Report Dr. S. G. Willimott gives an account of the method of administering the Food and Drugs Law in Cyprus. For this purpose the Island is divided into seven districts. Adulteration was highest in Nicosia and Paphos districts, whilst in the districts of Kyrenia and Polis it was apparently non-existent. The general adulteration rate (3·6 per cent.) showed a marked decline on that of 1934 (23·9 per cent.), but this is believed to be only partly accounted for by any real drop in the amount of adulteration, and to be due principally to the fact that no special surveys and inspections of suspected stocks or old supplies of canned foods were made by the sanitary staff.

Of the 1310 samples examined, 48 were adulterated, namely, flour 25, olive oil 19, flour 2, milk 1, and condensed milk 1.

Condensed Milk Regulation.—By an Order in Council, No. 1634 of 1935, the importation of skimmed milk or of milk with a fat-content of less than 7 per cent. was prohibited. This was due to the fact that the uninformed poor in town and village have used this product, because of its lower price, for feeding infants.

Adulteration of Olive Oil.—An important test case of adulteration of olive oil was heard before the President of the District Court, and the vendor was heavily fined. On appeal to the Supreme Court the conviction and sentence were confirmed, and cancellation of Government contracts followed. Adulteration of olive oil, with all manner of cheaper vegetable oils, was rife during the year.

Use of Quinine as a Poison.—The use of quinine as a poison by would-be suicides is still not uncommon in Cyprus. In one case, in which a young Greek woman ingested 45 grains of quinine, traces of the alkaloid were found in the vomit and stomach washings.

Permanganate Poisoning.—An unusual case of poisoning with potassium permanganate was investigated. The distinguishing feature of the case was that the permanganate was not ingested *per os*, but self-injected through the urethral canal. The total amount of permanganate solution brought in contact with the tissues of the urethra and bladder was equivalent to 20 g. of the solid salt. The case ended fatally, and at the autopsy extensive burns of the mucous membrane of the bladder and urethra were found. Full details were published in the *British Medical Journal*, Jan. 11th, 1936, p. 58.

Local Manufacture of Hashish.—The hemp plant (*Cannabis sativa* L.) has been grown in the Island since Venetian days and probably a long time before that, and it is noteworthy that the names of at least two villages are derived from that of the cultivated plant. The plant is cultivated in the Paphos district as a field crop for its fibre, but the production of hashish is unknown and in any case

prohibited. During the year the Customs authorities submitted samples connected with an attempt, fortunately unsuccessful, to prepare hashish in the hemp-growing district. The attempt failed because extraneous material and crude appliances appeared to have been used. The laboratory findings on the material submitted were entirely negative.

MOSQUITOES AND WATER SALINITY.—In conjunction with the survey of malaria in Cyprus by the Rockefeller Foundation a number of observations on brackish waters from different malarial localities have been made. In particular, samples from the Larnaca salt lakes were analysed for salinity and reaction, in an attempt to correlate these figures with the presence of eggs, larvae or pupae of species of mosquito maturing there. It appears that two species, *multicolor* and *elutus*, have different critical salinity points beyond which they cannot exist. On the Kyrenia coast an important observation has been made that eggs and larvae of *Aedes mariae* (fortunately not a malaria vector in Cyprus) can flourish in salt water of extraordinarily high salinity. This work is being continued in co-operation with the Foundation.

CYPRUS UMBER.—The umber and ochre beds are among the most interesting mineral resources of the Island, and the winning of the ore is probably of great antiquity. Ancient slags have been found to contain considerable amounts of manganese, but whether the Phœnicians and Romans used the umber, which was easily accessible, as a flux in smelting their pyrites for copper, remains a matter of debate. The umber beds occur on the line of contact of the pillow lavas with the overlying marls and sedimentaries. The question of the geological origin of the umber beds in Cyprus cannot be discussed here, but it is very doubtful whether the theory of contact metamorphism of Gaudry can be accepted (*cf.* C. G. Cullis and A. B. Edge: *Cupriferous Deposits in Cyprus*, London, 1927). Geological study of the question shows, however, that the natural deposits of the umber must be enormous, and are for the most part untapped.

At Larnaca, the seat of the industry, the ore is exported as raw umber in lumps and as burnt umber in powder, and may be graded into 25 different shades. The colour of the natural umber varies from yellowish-brown to dark sepia, according to the manganese-content, which has been found to range from less than 1 up to 10 per cent. It is well known that manganese salts are readily leached out of rocks by percolating water, so that the manganese-content of any particular specimen appears to vary according to whether its position in the umber bed was above or below the geological water table. The subject is by no means one of academic interest only and, so far as our experience goes, the results appear to confirm this theory.

Specimens of Cyprus terra verta, which occurs in small pockets in the contact zone, have also been analysed and found to be free from arsenic and copper. The colour is due to the mineral chlorite.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Composition of Pineapples. J. C. Bodenstein. (*Union of South Africa, Dept. of Agriculture and Forestry, Science Bull.*, No. 153, 1936.)—Samples of pineapples were bought in Johannesburg at different times from September to March, 1933–4. Bulk samples A, B, C, D consisted of 20, 24, 11, and 19 fruits, respectively. Each fruit was weighed when received and when cut up for analysis, and the results were corrected for the loss of moisture between these times. An almost clear juice was obtained by cutting the fruit into slices, about ½ in. thick, and pressing each separately in a powerful screw-press. Sugars, specific gravity and acidity were determined immediately after squeezing out the juice. Ash and nitrogen were determined later on samples sterilised by heating in bottles in a water-bath at 70° C. for 1 hour, and adding a small crystal of thymol; these were tightly corked and sealed with paraffin wax when hot. *Analysis.—Alcohol-insoluble residues* were determined by Copeman's method (*Trans. Roy. Soc. S. Afr.*, 1931, p. 107), which has been successfully used for jams (Macara, ANALYST, 1931, **56**, 35). *Soluble solids* were calculated by means of the formula

$$W = \frac{1000\,(D - 1{\cdot}000)}{3{\cdot}85}$$

where D represents the sp.gr. of juice at 20° C., and W the number of grams of soluble solids per 100 ml. of juice. *Density* was determined at 20° C. in a 25-ml. specific-gravity bottle. *Sugar-content of the juice* was found by a method based on that of Evans ("Chemical Studies in the Physiology of Apples," Part VII, *Ann. Bot.*, 1928, **42**, p. 1). The juice was clarified with a saturated solution of normal lead acetate, and the excess of lead was removed by means of potassium oxalate. The juice was clarified for the determination of glucose and fructose; no significant difference in the total sugars was found between clarified and unclarified juice. Reducing sugar in the dilute clarified solution was determined before and after inversion by the method of Lane and Eynon (*J. Soc. Chem. Ind.*, 1923, **42**, 32; Abst., ANALYST, 1923, **48**, 220). Reducing sugar originally present was returned as invert sugar, the difference between amounts present before and after inversion being calculated as sucrose. These methods gave considerably lower results than those of Davies, who determined the sugar after sterilising the juice at 70° C. for 1 hour. Further experiments showed that inversion occurred during sterilisation. *Glucose and fructose* were determined by the method of Hinton and Macara (ANALYST, 1924, **49**, 2); *acidity* was calculated as citric acid; *nitrogen* was determined by the Kjeldahl method, copper sulphate being used as a catalyst, and 5-ml. samples taken to save time in digesting. *Ash*: Fifty ml. were evaporated on a water-bath, and the residue was charred on a hot-plate and ignited at low red-heat in an electric furnace. It was then treated with dilute hydrochloric acid, evaporated to dryness, and kept at 110° C. for 1 hour, to render silica insoluble;

the soluble portion was then extracted with water acidified with hydrochloric acid, the extract was filtered, and the insoluble residues from three bulk samples were ignited and weighed together in a small platinum crucible. The soluble portion was made up to 100 ml. and used for the determination of potash, lime, magnesia, phosphate, and manganese oxide. *Potash* was determined in 5 ml. by Milne's volumetric cobaltinitrite method (*J. Agric. Sci.*, 1929, 541; Abst., ANALYST, 1929, **54**, 558). *Lime* was determined on 50 ml., by boiling with 0·5 g. of ammonium acetate, precipitating with ammonium oxalate, filtering after standing overnight, and titrating the precipitate with standard permanganate solution. *Magnesia* was determined in the filtrate and washings by precipitation with sodium ammonium phosphate after evaporation to about 50 ml. Complete precipitation was easily attained, owing to the high magnesium-content of the ash. After standing overnight, the precipitate was filtered off and dried at 50° to 60° C. to remove traces of ammonia, and magnesia was determined by adding a definite amount of standard sulphuric acid and titrating back with alkali. *Phosphate* was determined colorimetrically by Lonstein's molybdate method (*S.A. J. Sci.*, 1926, p. 185). *Manganese* was determined in 25 ml. of the acid solution of the ash, after removal of chlorides with silver nitrate. The method was the usual colorimetric one depending on oxidation to permanganate by means of persulphate. The results agreed well with those obtained by removal of chlorides by evaporation with sulphuric acid.

The ratio of fructose to glucose was from 0·73 to 0·85 on the four bulk samples analysed. Malic acid, as well as citric acid, was sometimes present in the juice. Exceptionally high potash values corresponded with exceptionally low lime values and *vice versa*. The manganese-content varied greatly for different samples and for individual fruits in each sample, and no relation between it and any other observed factor could be traced. For all tests, tables are given of results for the bulk samples, with standard deviation, and coefficient of variation. The significance of results and the relation between them is discussed. The results, relating to expressed juice, were as follows:

Insoluble residue, g.	per 100 g.	3·00	to	3·32
Soluble solids, g. ..	per 100 ml.	16·24	to	18·93
Sucrose	,, ,,	10·80	to	12·89
Reducing sugars ..	,, ,,	2·73	to	3·13
Acidity (as citric acid)	,, ,,	1·01	to	1·05
Nitrogen in juice ..	,, ,,	0·038	to	0·046
Ash in juice ..	,, ,,	0·360	to	0·448
Potash	,, ,,	0·176	to	0·239
Lime	,, ,,	0·0142	to	0·0124
Magnesia	,, ,,	0·0282	to	0·0329
Phosphoric oxide ..	,, ,,	0·0071	to	0·0107
Manganese, as Mn_3O_4, mg.	,, ,,	0·68	to	1·65

E. B. D.

Control of the Ripeness of Table Grapes in the Avignon Region. G. Mathieu. (*Ann. Falsificat.*, 1936, **29**, 355–356.)—The following results (*inter alia*) are given, in confirmation of those obtained by Hugues and Bouffard

(ANALYST, 1936, 619); the sugar is given in g. per litre and the acid as g. of tartaric acid per litre of must:

Cavaillon.—Sweet water variety. Vineyard on the plain.

	Date	Sample	Sugar	Acid	Ratio Sugar:acid	Taste
1933	August 18th	1	126	5·85	21·5	edible
		2	128·5	5·7	22·5	pleasant
		3	135	5·1	26	quite ripe
	August 21st	1	129	6·1	21	somewhat acid
		2	132	5·5	24	pleasant
		3	135	5·35	25	pleasant
		4	154	4·35	35	very ripe
	August 25th	1	139·5	4·95	28	ripe
		2	166	4·3	39	very ripe

Cavaillon.—Sweet water variety.

	Date	Sample	Sugar	Acid	Ratio Sugar:acid	Taste
1934	August 7th	1	121	7·3	16·5	sour
		2	127	6·9	18·5	sour
		3	138·5	6·35	22	edible
	August 13th	1	123	6·85	18	sour
		2	135	6·5	21	just edible
		3	139	6·15	22·5	edible
	August 16th	1	128·5	6·65	19	sour
		2	134	6·3	21	pleasant
		3	142	5·8	24·5	ripe

Cavaillon.—Sweet water variety.

	Date	Sample	Sugar	Acid	Ratio Sugar:acid	Taste
1935	August 11th	1	124	7·25	17	sour
		2	159	6·65	24	ripe
	August 12th	1	124	7·5	16·5	sour
		2	167	5·3	31·5	very ripe
	August 17th	1	122	6·9	18	sour
		2	129	6·55	20	somewhat acid
		3	138	6·2	22	pleasant
		4	141	6·15	23	pleasant

Judged by the samples examined the grape is edible when the sugar : acid ratio in the must is 20 or slightly higher, but the fruit is still too acid to be acceptable to all palates. The grape is pleasantly sweet when the ratio is 25 or more, and perfectly ripe when the ratio is about 30. It is suggested that the grapes should not be sold with a sugar : acid ratio of less than 25. E. M. P.

Detection of Sucrose in Vegetable Material. K. Täufel, H. Thaler and G. Kopp. (*Z. Unters. Lebensm.*, 1936, **71**, 390–393.)—Exhaustive acetylation of sucrose converts it into the octo-acetyl derivative, which is insoluble in hot and cold water, but readily soluble in ether and chloroform. This affords an easy method of separating sucrose from other substances occurring in vegetable matter, and by saponification of the acetyl derivative by means of sodium methoxide (Zemplén, *Ber.*, 1926, **59**, 1258) the sucrose can be recovered in aqueous solution.

The process has been applied successfully to sucrose occurring in coffee beans and in malt. The de-fatted raw coffee (250 g.) is heated with 2 litres of 80 per cent. alcohol beneath a reflux condenser for an hour. The extract is filtered while hot and the residue is treated in the same manner with two 1-litre portions of 80 per cent. alcohol for half-an-hour. The combined extracts are evaporated, the dry residue is dissolved in water, and the dark solution is clarified by means of lead acetate, the excess of lead being removed by means of sodium sulphate solution. After filtration the solution is evaporated *in vacuo* and the residue dried over phosphorus pentoxide until it can be pulverised. The yield is about 50 g. Twenty g. of the finely pulverised extract are mixed by trituration with 60 g. of freshly-dehydrated powdered sodium acetate and heated beneath a reflux condenser with 150 ml. of freshly-distilled acetic anhydride for 6 hours, a little pipe-clay being added to prevent bumping. The hot mixture is poured into 500 ml. of hot water, under a hood, with constant stirring. The black, supernatant liquid is decanted from the insoluble residue, which is washed by stirring with 500-ml. portions of boiling water until free from the odour of acetic acid. It is then superficially dried, and dissolved in ether, and the solution filtered. Large crystalline scales may be obtained by concentration of the ethereal solution at room temperature. After evaporation of the ether the residue is washed by stirring three times with boiling water, to remove the last traces of ether, which clings stubbornly to the compound, and is finally dried over phosphorus pentoxide. The yield is about 4·5 g. of a brown lacquer-like mass. Determination of the number of acetyl groups confirms its identity. For saponification, 4 g. of the derivative are dissolved in 100 ml. of dry chloroform, and the solution is cooled to −20° C., after which 10 ml. of a solution of 1 g. of sodium in 50 ml. of methyl alcohol, cooled to the same temperature, are slowly added. Cooling is maintained, and the liquid is agitated until it sets into a jelly which is allowed to remain in the cooling-bath for 5 minutes longer. Twenty ml. of water are added, the mixture is shaken vigorously and, after neutralisation with dilute acetic acid, the aqueous layer is separated from the chloroform layer and concentrated *in vacuo*. By treatment of the syrup with a mixture of 5 parts of alcohol and 1 part of ether a white precipitate is formed; this is filtered off, dissolved in boiling 80 per cent. alcohol and allowed to crystallise. The crystals are identified as sucrose by determination of their melting-point and optical rotation. The procedure for malt is as follows:— One kg. of green malt is treated, in two portions, with 5 litres of 80 per cent. alcohol for 6 hours beneath a reflux condenser. The yellow filtrate is neutralised with sodium hydroxide solution, the alcohol is distilled off, and the proteins are separated by treatment with lead acetate, the excess of lead being removed with sodium sulphate. Reducing sugars are then removed by heating 500 ml. of the aqueous solution on the water-bath with 600 g. of barium hydroxide dissolved in about 800 ml. of water and 2 litres of 3 per cent. hydrogen peroxide for half-an-hour. The liquid is then filtered and the dissolved barium hydroxide is removed by means of a stream of carbon dioxide. Absence of directly reducing sugars in the final filtrate is ascertained by means of Fehling's solution. The liquid is concentrated *in vacuo* at 40° to 42° C., and the yellow residue is dried over phosphorus pentoxide for 2 days and for a further 2 days in a drying-oven at 55° to 60° C.

The yield is about 30 g. of a somewhat viscous solid. This is treated with 90 g. of sodium acetate and 225 ml. of acetic anhydride beneath a reflux condenser for 7 hours. The hot dark liquid is poured into a litre of hot water, and the dark sediment (yield about 4 g.) is purified as previously described. Saponification of the derivative is carried out in the manner described for coffee. The final product consists of characteristic, though somewhat yellow, crystals of sucrose.

A. O. J.

Magnesium Laurate Test for Coconut and Palm-kernel Oils in Butter-fat. E. Tchetcheroff. (*Ann. de Gembloux*, 1936, 204–205.)—Grossfeld (*Z. Unters. Lebensm.*, 1928, **55**, 529; Abst., ANALYST, 1928, **53**, 603) based tests for coconut and palm-kernel oils upon the fact that they contain about ten times as much lauric acid as butter-fat. One of these tests depended upon the difference in the solubilities of magnesium laurate in hot and cold water, and it is now shown that the method can be used qualitatively. The amount of fat taken is 2·5 to 2·6 g., and Grossfeld's reagents (*loc. cit.*) are modified as follows:—For the saponification an approximately $N/2$ solution of potassium hydroxide in 90 per cent. ethyl alcohol is used. The solution of magnesium sulphate contains 50 g. per litre (in place of Grossfeld's 1·5 per cent. solution). The insoluble magnesium soaps, precipitated from the saponified fat, are filtered off and washed with water at 30°–40° C. into a tared Erlenmeyer flask, and the weight is made up to 250 g. by the addition of water. Fifty ml. of the suspension (which has been thoroughly shaken) are transferred to a beaker, mixed with 50 ml. of water and 10 ml. of glycerin solution (300 g. per litre), and boiled for a short time. The boiling liquid is poured on to a filter in the bottom of which is a pinch of kieselguhr, and the filtrate is allowed to stand. Magnesium laurate, if present, separates in characteristic flocks. Butter-fat contains so little lauric acid that no flocks appear, even after 12 hours' standing. The method is capable of detecting 5 per cent. of coconut or palm-kernel oil in butter.

Balsam Pear Seed Oil. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 220–221B.)—One of the two new stereoisomers of elaeostearic acid reported to be present in the oil of *Trichosanthes cucurmeroides* has now been identified in the seed oil of the balsam pear, *Mormordica charantia*, L. The seeds (averaging 0·175 g.) contained 65 per cent. of kernels, yielding, on extraction with ether, 40·89 per cent. of an orange-yellow oil, with the following characteristics: sp.gr. at 40/4° C., 0·9153; n_D^{40}, 1·5010; m.p., 26°–27° C.; saponification value, 189·9; iodine value (Wijs), 140·1; acid value, 0·63; and unsaponifiable matter, 0·91 per cent. The drying power of the oil was somewhat less than that of *Trichosanthes cucurmeroides* oil. The solid fatty acids were separated by means of magnesium acetate in 90 per cent. alcohol (*J. Amer. Chem. Soc.*, 1923, **45**, 113; Abst., ANALYST, 1923, **48**, 126), and fractionally crystallised from 80 per cent. alcohol into three fractions with iodine values of 121·1, 153·4 (m.p. 56°–57° C.) and 187·8 (n_D^{50}, 1·5100; m.p., 30°–33° C.), respectively. The third fraction consisted mainly of trichosanic acid (m.p., 35°–35·5° C.; sp.gr., 50/4° C., 0·9025; n_D^{50}, 1·5113; neutralisation value, 200·0; iodine value, Wijs, 202·1), and the pure acid was also obtained from the filtrate from the insoluble magnesium soaps.

D. G. H.

Chemical Examination of the Fixed Oil from the Seeds of *Celastrus paniculatus* Willd. O. N. Kumaraswamy and B. L. Manjunath. (*J. Indian Chem. Soc.*, **1936**, **13**, 353–357.)—The shrub *Celastrus paniculatus* (N.O. *Celastrineae*) is found in Bihar, Bengal, Burma, and Ceylon ("Indigenous Drugs of India," K. L. Dey, 1896, 74; "Indian Materia Medica," Nadkarni, 1927, 187), and its seeds yield an oil "said to be a sovereign remedy in beri-beri," a nerve stimulant and a brain tonic. In Ayurvedic and Unani medicines the seeds and oil are prescribed for rheumatism, gout, paralysis, and leprosy. The crushed seeds were successively extracted with various solvents and yielded the following percentages of extract:—Petroleum spirit (thick brownish-yellow oil of unpleasant taste), 52·2; ethyl ether, 1·6; chloroform, 0·5; ethyl acetate, 0·4; and alcohol, 2·8 (viscous, highly-coloured substance). No alkaloid was detected in the seeds. The extracted fatty oil had the following characteristics:—sp.gr. at 25/25° C., 0·9586; n_D^{30}, 1·4747; saponification value, 239·2; iodine value (Hanus), 102·9; Reichert–Meissl value, 62·8; acetyl value, 130·1; Hehner value, 75·2 per cent.; acid value, 44·4; unsaponifiable matter, 5·7 per cent. *Mixed fatty acids*: mean mol. equiv., 275·3; iodine value (Hanus), 112·6. Treatment of the mixed fatty acids by the lead-salt method yielded 30·54 of saturated acids of mean mol. wt., 264·0, iodine value (Hanus), 1·8; and unsaturated acids of mean mol. wt., 335·7; and iodine value, 154·9. The unsaturated acids were found by bromination treatment and alkaline oxidation to contain oleic, linolic and linolenic acids. Fractionation and recrystallisation of the five fractions previously separated showed the saturated acids to contain palmitic, cerotic, stearic and lignoceric acids. Acetic acid and a small quantity of benzoic acid were also identified. Only a small quantity of a phytosterol could be isolated from the unsaponifiable matter, the main bulk, after a number of crystallisations from acetone, giving a granular, neutral, non-nitrogenous material, m.p. 61°–65° C., which gave negative results in tests for hydroxyl and carbonyl groups and gradually resinified. D. G. H.

Composition of some Solanaceous Seed-fats. T. P. Hilditch and M. B. Ichaporia. (*J. Soc. Chem. Ind.*, **1936**, **55**, 189–190T.)—The general characteristics of the oils extracted by means of petroleum spirit from the seeds of (1) *Datura stramonium*, (2) *Atropa belladonna*, and (3) *Hyoscyamus niger* were as follows:—saponification equivalents, (1) 287·0, (2) 296·7, (3) 290·3; iodine values, (1) 115·8, (2) 146·5, (3) 151·0; acid values, (1) 6·7, (2) 28·0, (3) 27·0; unsaponifiable matter, (1) 1·9, (2) 2·5, and (3) 0·3 per cent. Distillation of the methyl esters of the solid and liquid acids showed the component fatty acids of the three oils to be as follows:—myristic acid, (1) 1·3 (?); palmitic, (1) 10·8, (2) 5·9, (3) 6·5; stearic, (1) 1·2, (2) 1·8, (3) 0·4; oleic, (1) 33·1, (2) 25·5, (3) 11·1; and linolic, (1) 53·6, (2) 66·8, (3) 82·0 per cent., respectively. Oxidation of the unsaturated acids from the ester fractions richest in C_{18}-unsaturated esters by the alkaline permanganate method, showed that *Datura stramonium* yielded tetrahydroxystearic acids, m.p. 152°–153° C. and 170°–172° C.; *Atropa belladonna*, tetrahydroxystearic acids of m.p. 154°–155° C., and 170°–171° C. (addition of bromine gave a tetrabromostearic acid m.p. 112°–113° C., sparingly soluble in petroleum spirit); and *Hyoscyamus niger* acids gave, on bromination, the tetrabromostearic acid of m.p. 112°–113° C.

Linolenic acid was not found in any of the three oils. The general glyceride structure of the *Datura stramonium* oil was studied by partial hydrogenation, and the glycerides were found to be assembled on the lines characteristic of nearly all the seed-fats so far examined. The figures for the component acids of this oil agreed closely with those previously recorded. D. G. H.

Chemical Analysis of Pyrethrum. J. Ripert. (*Ann. Falsificat.*, **1936**, **29**, 344–354.)—The solubility in petroleum spirit of the pyrethrins in pyrethrum flowers decreases during storage, probably owing to the development around the pyrethrin globules of envelopes of oxy-acids formed by oxidation of fatty acids. Comparative experiments with petroleum spirit and chloroform as solvents for the extraction of pyrethrins from dried pyrethrum flowers and pyrethrum powders show that more complete extraction is obtained with chloroform than with petroleum spirit. The percentage results are embodied in the Table.

Solvent	Seyl's method: Without neutralisation of pyrethrins I	II	Total	Seyl's method: With neutralisation of pyrethrins I	II	Total
Petroleum spirit	3·2	5·2	8·4	3·2	4·61	7·81
Chloroform	4·5	8·9	13·4	4·29	7·04	11·33
Chloroform after petroleum spirit	1·37	4·21	5·58	1	2·85	3·85

Solvent	Ripert's method pyrethrins I	II	Total	Semi-carbazone method Total pyrethrins	Methoxyl method pyrethrin II
Petroleum spirit	3·6	4·3	7·9	9·4	5·1
Chloroform	4·9	7	11·9	13·2	9·8
Chloroform after petroleum spirit	1·28	2·21	3·49	4·2	4·49

Present methods of analysing pyrethrum powders and commercial products containing pyrethrins depend on the properties of chrysanthemic acids, one such method being that of Seyl. A method recently proposed by Haller and Acree (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 343) for the estimation of pyrethrin II is based on the determination of the methoxyl group therein by Zeisel's method, using a crude petroleum spirit extract; the new method always gives results lower than those obtained by Seyl's method. The author has developed the method based on the use of semi-carbazide, the procedure being as follows:—The solvent is removed by evaporation in a vacuum from the extract to be analysed, and the residue is taken up in pure absolute alcohol containing an excess of semi-carbazide. After standing for 36 hours at 30° C. the alcohol is evaporated *in vacuo*, the residue is taken up with chloroform, and the solution is washed with water to remove uncombined semi-carbazide, and dried over sodium sulphate. The chloroform is evaporated until the residue attains constant weight. Nitrogen is determined by Pregl's (micro-Dumas) method in the material thus extracted, and the pyrethrin-content is calculated, its molecular weight being taken as the average of the molecular weights of pyrethrin I and pyrethrin II. The author has compared these various methods, the results of the comparison being given in the foregoing Table. Graham (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 222), in a paper on the

analysis of perfumed insecticides, in which the pyrethrins are in solution in petrol, states that there is a loss of 25 per cent. of the total pyrethrin when the perfume is removed in steam by Seyl's method prior to the analysis. The author cannot confirm Graham's results, for he has repeatedly found that when 500 ml. of insecticide are used for the analysis no perceptible loss of pyrethrin occurs during the steam-distillation, and that even when the distillation is prolonged the loss is much smaller than that obtained by Graham. The results of these experiments are given in detail. E. M. P.

Notes on *Strophanthus dichotomus*, D.C. A. H. Millard. (*Pharm. J.*, 1936, **137**, 147–149.)—*Toxicity.*—A tincture was made from seeds freed from oil by extraction with petroleum spirit. The seeds were then digested with 70 per cent. alcohol for 24 hours at room temperature (about 30° C.), and the extract was filtered through a cotton-wool plug. The alcohol was evaporated, and an equal volume of 0·6 per cent. sodium chloride solution (A) was added to the residue. Solutions of various strengths were made by dilution with (A). Experiments with frogs showed the presence of a powerful cardiac poison. *Chemical Tests.*—These were made in comparison with seven other varieties of *Strophanthus*. An alcoholic tincture, which was grass-green in colour, prepared as described above, and equivalent to 2·5 per cent. of the untreated seeds, was used. This was evaporated on the water-bath and tests were made on 1-ml. portions of the residue, the following colour reactions being observed:—(*a*) 75 per cent. sulphuric acid: brown-violet in 10 to 15 minutes; (*b*) phosphomolybdic and sulphuric acids: emerald green; (*c*) aqueous phosphomolybdic acid: emerald green; (*d*) sodium tungstate and sulphuric acid (or tungsten trioxide and sulphuric acid): green, changing to pink-violet; (*e*) vanadium pentoxide and sulphuric acid: brown, changing to greenish-brown; (*f*) ferric chloride and sulphuric acid: dirty green; (*g*) potassium dichromate and sulphuric acid: greenish-brown to green; (*h*) aqueous potassium dichromate and sulphuric acid: dirty pale green; (*i*) dilute nitric acid: no change; (*j*) phenol and hydrochloric acid: pink to cloudy bluish-green; (*k*) phenoldisulphonic acid: reddish-brown to dark violet; (*l*) furfuraldehyde and sulphuric acid, green, changing to brown-violet; (*m*) resorcinol and hydrochloric acid: pink-brown to red-orange; (*n*) Keller–Killiani reaction: brown ring, brown on mixing. Test (*a*) differentiates the tincture of *S. dichotomus* from all except those prepared from *S. Emini* and *S. Nicholson*. These latter tinctures give a violet colour with (*j*) and a purple one with (*m*). E. B. D.

Microscopy of Powdered Desiccated Endocrine Glands. P. A. Mattis. (*Amer. J. Pharm.*, 1936, **103**, 276–302.)—Methods of staining and mounting powdered endocrine glands are fully described. In bulk staining, dilute solutions are best. A list of twenty-eight stains used is given. (Of these, some were discarded.) The best are (*a*) Borrel's methylene blue in conjunction with eosin, (*b*) methylene blue and eosin, (*c*) silver nitrate (1 per cent.), (*d*) acid fuchsin and picro-carmine, (*e*) gold chloride (1 per cent.), (*f*) osmic acid (1 per cent.), (*g*) ammonium picrate, (*h*) Mallory's triple connective tissue stain, (*i*) Delafield's hematoxylin, and (*j*) Ponceau S (Curtis's substitute for Van Giessen's stain). Reagents which bring out certain features of the powders well are 20 per cent.

sulphuric acid, 2 per cent. acetic acid and potassium picrate. The best methods are the watch-glass method and the smear method for permanent preparations; the watch-glass method may also be used in staining for temporary mounts. The preparations examined were ovary, corpus luteum, thyroid, and pituitary (whole).

Ovary Preparations.—Features of diagnostic value include ova, particles of thecal follicles (with or without granulosa cells still adherent), lutein cells, and ovarian stroma with stellate connective tissue cells and rounded or beaked cells, the latter sometimes acidophilic (Plate A). Ovarian residue may be distinguished

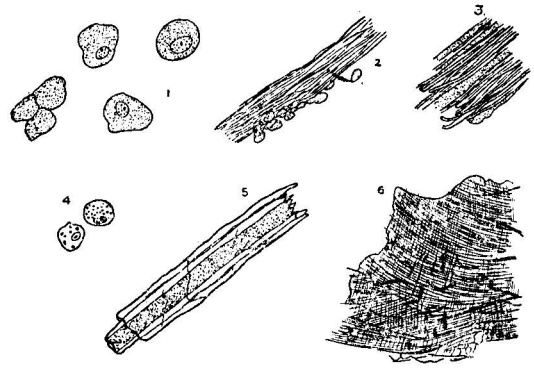


PLATE A. POWDERED DESICCATED WHOLE OVARY

(1) Lutein cells. (2) Portion of theca folliculi, showing cells of the stratum granulosum still adhering. (3) Unmyelinated nerves in ovarian tissue. (4) Ovarian stroma cells (note beaked cell). (5) Portion of myelinated nerve. (6) Connective tissue from the medulla.

from whole ovary by the presence of relatively greater amounts of connective tissue. Constituents of ovary preparations are stained as follows:—*Ovum nucleus* is stained dark purple by Delafield's stain (*i*) diluted with an equal volume of water, followed by an aqueous solution of eosin. *Thecal follicle* fibrils are stained pink by eosin, red by acid fuchsin, and blue by Mallory's stain (*h*). With Borrel's methylene blue and eosin they are stained deep blue against a bright pink background. *Lutein cells*, when stained with Delafield's stain (*i*), show a light purple small, rounded nucleus, whilst the cytoplasm is stained faint purple to pink. With Borrel's methylene blue (*a*) and eosin the nucleus is stained bright blue and the cytoplasm pink to purple. Some of the cells may show fat droplets, which are stained black with osmic acid; connective tissue is stained blue by Mallory's stain (*h*). In 2 per cent. acetic acid, collagenous fibres were swollen and elastic fibres untouched; in potassium picrate the elastic fibres stood out as wavy, yellowish strands.

Corpus luteum.—Mounts may show numerous isolated lutein cells, usually ovoid or polyhedral, and frequently containing a prominent nucleus. In Borrel's methylene blue (*a*) and glycerin mounts these cells are stained from blue to greenish-blue. Masses of lutein cells occur, usually with more or less connective tissue attached. Occasionally cells found in the theca may occur, still attached to the luteal mass, so that the whole of the connective tissue appears yellow and granular. The connective tissue shows the same staining reactions as that of the whole

ovary. Clear hyaline fragments (stained blue with Borrel's methylene blue, and dark brown with 1 per cent. silver nitrate solution) may also be noted.

Powdered desiccated thyroid.—This may be recognised by (1) the presence of follicular tissue and (2) the large amount of colloid (Plate B). The colloid is

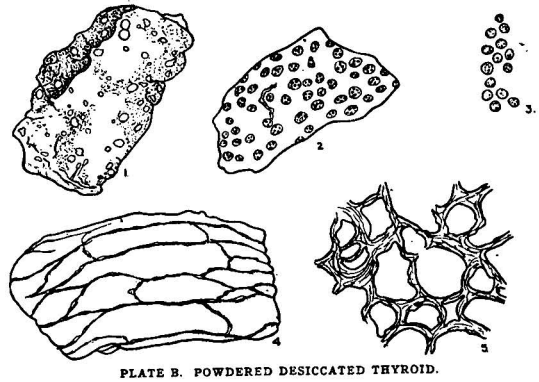


PLATE B. POWDERED DESICCATED THYROID.

(1) Colloid fragments, showing granules, a few cells and vacuoles. (2) Follicle wall, showing nuclei of follicular cells. (3) Isolated follicular nuclei, showing nucleoli. (4) Follicles and connective tissue (lateral view). (5) Follicular tissue (cross-sectional view).

usually stained dark purple to dark blue by Borrel's methylene blue (*a*) in smear preparations, sometimes light blue to purple; it was very light blue in temporary mounts with Borrel's methylene blue, light yellowish to deep reddish-brown in the 1 per cent. silver nitrate method, and bright yellow with picrocarmine. Follicle cells showed deep blue nuclei and lighter blue cytoplasm with Borrel's methylene blue; in smear preparations they showed deep purple to blue nuclei and pink cytoplasm.

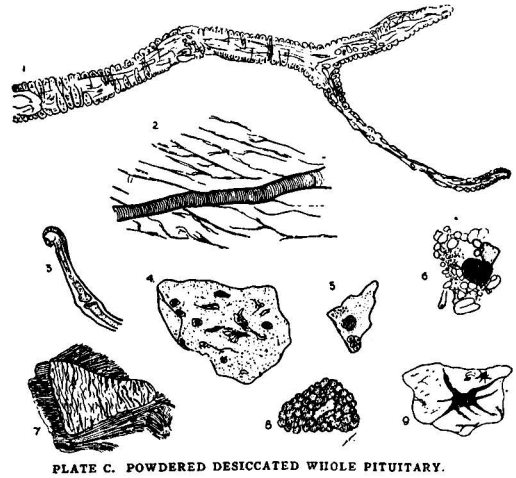


PLATE C. POWDERED DESICCATED WHOLE PITUITARY.

(1) Small arteriole. (2) Fragment from anterior lobe (pars distalis), showing capillary in tissue. (3) Myelinated nerve. (4) Fragment of pars nervosa. (5) Colloid inclusion in fragment of pars nervosa. (6) Small follicle, showing colloid. (7) Portion of fibrous capsule. (8) Group of cells from pars distalis. (9) Isolated glial cell.

Pituitary (*whole*) shows (1) three types of cells characteristic of the anterior lobe (pars distalis)—the chromophile (α- and β-cells) and chromophobe cells, (2) bits of cord-like tissue, (3) small pieces of colloid, and (4) neuroglia cells combined with neuraxons (Plate C). The smear method is used and careful observations are required. In smear preparations, chromophile cells are stained deep blue with (*a*), the α-type give bright red cytoplasm and the β-type pale blue; the pars distalis chromophobe cells give deep blue nuclei and faint pinkish cytoplasm with (*a*). Colloid fragments are stained pink with eosin, and black to dark brown with (*c*). Neuroglia cells are stained black with silver nitrate (*c*) and deep blue with methylene blue (*a*).

Other microscopic structures and stain-reactions are also fully described, and there are 21 figures. The test for trihydroxy-oestrin (theelol), namely, an orange colour, green fluorescence on standing, when an alcoholic extract is acidified with conc. sulphuric acid, is considered characteristic of whole ovary only. E. B. D.

Erratum:—*Assay of Lobelia*, September issue, p. 621, *for* "giving concordant results in agreement with the methods of Vanderkleed and E'We and of Mascre," *read* "results more concordant and accurate than". . .

Biochemical

Meta-dinitrobenzene as Indicator of the Respiration of Plant and Animal Cells. S. C. J. Olivier and K. Ebes. (*Rec. Trav. Chim. Pays-Bas*, 1936, **55**, 723–726.)—The germinative faculty of wheat and rye has been determined by treating the grains with *m*-dinitrobenzene in the presence of water for 5 hours at atmospheric temperature, or for 1 hour at 40° to 45° C., and then with dilute ammonia solution, and examining them under the microscope or with a lens after 10 minutes (Gurewitsch, *Ber. deut. botan. Ges.*, 1935, **53**, 303). In the botanical laboratory of Wageningen pure *m*-dinitrobenzene failed to give a violet colour, and it was found that the colour depends on the presence of small amounts of the *ortho*- and *para*-isomers as impurities. The *meta*-compound should therefore be replaced by one of these isomers, a very small amount being used. Excellent results have been obtained with 0·010 g. of either compound per 100 grains of wheat in 50 ml. of water. The *para*-compound alone gives an orange-red colour, the *ortho*-compound a colour tending to violet, and the two in impure *m*-dinitrobenzene, or when mixed, a dirty violet.

Test for isomers in m-*dinitrobenzene.*—The following test has been based on these observations:—About 0·5 g. of the powdered preparation and 5·5 g. of fresh bakers' yeast are shaken for some time with 50 ml. of water and allowed to stand for a few hours. After decantation, a few drops of dilute ammonia solution are added, the presence of the *ortho*- or *para*-compound, or both, being indicated by a dirty violet colour as described above. E. B. D.

Ammonium Sulphate Serum of Milk for Serological Investigations. H. Kluge. (*Z. Unters. Lebensm.*, 1936, **71**, 405–410.)—The serum obtained by removing casein from milk with ammonium sulphate solution contains albumin and globulin and, since the antigens and antibodies in milk are associated with

the globulin, this serum should be suitable for serological investigations. Fifty ml. of milk are treated with 2 drops of 30 per cent. acetic acid and 10 g. of crystallised ammonium sulphate, and the mixture is kept at room temperature and occasionally shaken until the salt is completely dissolved. If a clear filtrate is not now obtainable, more ammonium sulphate is cautiously added. In this way a serum is obtained which is quite clear and contains a considerable amount of albumin, the presence of which may be confirmed by the heat test. One of the objects of this investigation is to examine the possibility of using normal antisera obtained by the injection of rabbits with blood serum in place of the special antisera prepared by injection with the milk of the animal concerned. The milk serum, obtained as described, is diluted with 12 times its volume of water to destroy the salting-out action of the ammonium sulphate. The reaction is carried out in Ulenhuth serum tubes into which are placed 0·05-ml. portions of antiserum of titre 1 : 20,000 or 1-ml. portions of titre 1 : 10,000, and 0·5 ml. of the diluted milk serum is then added to each tube, the formation of separate layers being avoided. After the lapse of 5, 10 and 20 minutes the liquids in the tubes are examined for turbidity. The following results were obtained:—With the serum of cows' milk in the presence of normal bovine antiserum a distinct turbidity or a precipitate appeared. The normal antisera of pig and horse caused no turbidity, and the reaction with human antiserum was also wholly negative. Milk heated for half-an-hour at 65° C. yielded a serum in which the reaction with bovine antiserum was positive, and with horse, pig and human antisera negative. Similar positive reactions with bovine antisera were given by the serum of milk momentarily heated to 71° or 85° C., but the serum from boiled milk gave only a doubtful turbidity with bovine antiserum. The heat test indicated that albumin was present in the sera of the milks heated to 65°, 71° and 85° C., but absent from the serum of the boiled milk.

The diluted serum from human milk gave a distinct turbidity with normal human antiserum of titre 1:10,000, but remained quite clear with the antisera of ox, horse, pig, goat and sheep. Human milk, momentarily heated to 85° C., gave a positive reaction with human antiserum and a positive albumin test. By the foregoing procedure it was found possible to detect an addition of 10 per cent. of cows' milk to human milk, or an addition of 10 per cent. of human milk to cows' milk. Below 10 per cent. the turbidity was doubtful. The diluted serum of goats' milk gave a positive precipitin reaction with goat antiserum, but bovine antiserum also reacted with the serum of goats' milk. Similarly, cows' milk serum gave positive reactions with goat antiserum. The reaction varied with the specimen of goat antiserum used but, in general, this method cannot be used to distinguish goats' milk from cows' milk with certainty. The ammonium sulphate serum of milk may also be used for the differential diagnosis of bacterial species, since agglutinins occur in the globulin fraction of milk. The serum for this purpose is prepared by dissolving 10 g. of ammonium sulphate in 50 ml. of milk and filtering off the clear serum. The initial dilution is ten-fold, and further dilutions are made in geometrical progression, all dilutions except the first two (which are made with water) being made with physiological salt solution. In this work the progressive dilutions were 1: 10, 1: 20, etc., to 1:1280. As test object a loop of a fresh agar

culture of the bacterium was used. Observations of the clumping were made at three-fold magnification in an agglutinoscope after 2 to 24 hours' incubation at 37° C. By this method the agglutination reaction can be applied to the routine control of milk supply, milk serum being used instead of the less convenient blood serum. The reaction is applicable to milk preserved with formaldehyde, which increases its utility for routine testing. A large quantity of milk from healthy cows was divided into three portions—A, B, and C. Portions of 150 ml. of B were inoculated respectively with 0·15 ml. of concentrated typhoid antiserum (titre 1 : 100,000), concentrated paratyphoid antiserum (titre 1 : 20,000), and concentrated *B. abortus* Bang antiserum (titre 1 : 100,000). The portion C was treated with 3 drops of commercial formalin per 250 ml., and portions of it were then inoculated in exactly the same manner as B. The sera of A, B, and C were then prepared. Initially the undiluted serum was used and dilutions were made with water instead of physiological salt solution. In sample A there was no agglutination. The diluted sera of B and C produced agglutination in the corresponding cultures for typhus at a dilution of 1 : 64, for paratyphoid 1 : 32, and for the Bang bacillus 1 : 64. With milk serum from cows infected with *B. abortus* Bang agglutination occurred at a dilution of 1 : 640. It should be noted that, when this test is applied to detect infection with *B. abortus* Bang, a positive agglutination reaction shows that the cows either are or were infected, for the antibodies are detectable months, or even years, after infection. As a routine control method it should, therefore, be used in conjunction with veterinary inspection. In heated milk the agglutinins have been destroyed, but since *B. abortus* Bang is simultaneously destroyed, there is no danger of infection. A valuable use of the test is for the detection of the addition of milk infected with *B. abortus* to milk produced under veterinary inspection. A. O. J.

An Antirachitically Active Irradiation Product of 7-Dehydrocholesterol. A. Windaus, Fr. Schenck and F. v. Werder. (*Hoppe-Seyler's Z. phys. Chem.*, 1936, **241**, 100–103.)—7-Dehydrocholesterol in benzene solution was irradiated with the magnesium spark. After removal of unchanged material, treatment with petroleum spirit, citraconic anhydride and finally 3 : 5-dinitrobenzoyl chloride led to the formation of a crystalline dinitrobenzoate. From the hydrolysate of this material was isolated a substance showing a biological activity rather over half that of calciferol. This oily product had an absorption spectrum identical with that of calciferol, but could not be obtained crystalline; it was also obtained from the irradiated material by means of the allophanate. The authors designate this substance vitamin D_3. S. G. S.

Isolation of the Antirachitic Vitamin from Tunny-liver Oil. H. Brockmann. (*Hoppe-Seyler's Z. phys. Chem.*, 1936, **241**, 104–115.)—A concentrate from tunny-liver oil, obtained by removing the sterols from the unsaponifiable matter, was submitted to several treatments with methanol and petroleum spirit, and then to a series of adsorptions on aluminium hydroxide. The original concentrate contained 80 international units of vitamin *D* per mg.; the richest material separated contained 6700 international units per mg. From this was prepared a dinitrobenzoate identical in all respects with that separated

from the irradiation product of 7-dehydrocholesterol (see previous abstract). The analysis of the dinitrobenzoate gave a composition corresponding with a formula $C_{27}H_{44}O$ for the alcohol, identical with that of 7-dehydrocholesterol. The authors conclude that the "natural" vitamin *D* present in tunny-liver oil, therefore, is vitamin D_3, bearing the same relation to 7-dehydrocholesterol as calciferol bears to ergosterol. S. G. S.

Toxicological

Selenium-content of Wheat. W. O. Robinson. (*Ind. Eng. Chem.*, 1936, **28**, 736–738.)—Wheat containing 15 p.p.m. of selenium was found to be highly toxic to white rats (Munsell, De Vaney, and Kennedy, to be published by U.S. Dept. Agr.). Random selections of wheat grown in various parts of the world were found to contain from 0·1 to 1·9 p.p.m. of selenium. The maximum here is thought to be too low to be injurious to health, but investigation is required, particularly as samples of wheat from the same field vary considerably in toxicity. *Analysis.*—As nearly all the selenium is concentrated in the gluten, this was separated and analysed. Finely-ground wheat, made into dough with water, was kneaded in a bag under water to remove starch. The bran was then separated by flotation in water, and the gluten was dried, weighed, ground and analysed by a modification of the method of Robinson, Dudley, Williams, and Byers (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 274–276; *cf.* ANALYST, 1935, **60**, 270). Twenty-five ml. of water, 20 ml. of nearly saturated magnesium nitrate solution and a solution of 7 to 10 g. of potassium hydroxide in 40 ml. of water, were successively stirred into 25 g. of gluten in a 400-ml. silica dish. Each stirring was rapid and thorough. The dish was heated on the steam-bath until the upper surface of its contents was dry, though the bulk remained moist, and was then covered and heated in an electric furnace at 500° to 525° C. The rate of combustion was somewhat controlled by raising the cover frequently. After carbonisation, the cover was removed, and the mass was turned with a spatula and kept in the furnace for 15 to 20 minutes. From this point onwards, the original method was followed. *Results.*—For wheat from various districts, the selenium-content in p.p.m. was (*a*) New South Wales, 0·1 to 0·7; (*b*) Argentina, 0·4 to 0·8; (*c*) Saskatchewan, 1·9 (one sample); (*d*) San Jacinto, Mexico, 0·6 (one sample); (*e*) S. Africa, 0·2 and 1·5 (two samples); (*f*) Spain, 0·2 to 0·8; (*g*) United States, 0·1 to 0·3; (*h*) Canterbury Area, N.Z., 0·4 (one sample); (*i*) Hungary, 0·3 and 0·4 (two samples). These results may be too low, because up to 20 per cent. of the selenium may be lost in obtaining the gluten. Toxic wheat from a South Dakota field, and Hurd-Karrer's wheat grown on soil containing 5 p.p.m. of sodium selenate, showed the following distribution of selenium, in p.p.m.:

	Toxic field-grown wheat	Hurd–Karrer's wheat
Whole wheat	26	90
Gluten	121	340
Bran	22	94
Starch	5	7
Soluble and suspended matter ..	16*	180†

* 8·9 per cent. of wheat. † 7·2 per cent. of wheat (some loss).

Glutens prepared for special diets should be examined for selenium-content. A gluten purchased in New York contained 12 p.p.m. of selenium, and the gluten separated from wheat raised on artificially selenised soils contained 340 p.p.m. A gluten of this selenium-content would be dangerous to use, and one containing 16 p.p.m. could hardly be considered wholesome. E. B. D.

Inhibiting Effect of Sulphur in Selenised Soil on Toxicity of Wheat to Rats. A. M. Hurd-Karrer and M. H. Kennedy. (*J. Agric. Res.*, 1936, **52**, 933–942.)—As a result of investigations into a disease of livestock it has been stated that addition of 1 p.p.m. of selenium as sodium selenate to the soil concerned rendered wheat grown thereon toxic to wild rats (Nelson, Hurd-Karrer and Robinson, *Science*, 1933, **78**, 124), but that the quantity of selenium absorbed by the wheat could be reduced by increasing the amount of sulphur present in the soil (ANALYST, 1934, **59**, 842; *J. Agric. Res.*, 1935, **50**, 413). In the present experiments winter wheat grown on soil containing 2 p.p.m. of selenium (calculated on a depth of 6 inches) and comprising 70 per cent. of the diet of white rats, produced the retarded growth and liver injury characteristic of selenium poisoning; the remainder of the diet was skim-milk powder, dried bone and meat scrap, yeast powder, butter and cod-liver oil. Wheat was not toxic if grown on soil to which was added sulphur (at the rate of 1500 lbs. per acre, in the form of flowers of sulphur or of gypsum), followed after 2 days by selenium. Chemical analyses of the grain showed that the additions of sulphur had reduced the concentration of selenium in the grain from about 12 p.p.m. to about 4 p.p.m. Neither the plants nor the grain from the selenised plots differed in appearance from those grown on control plots receiving no selenium. White rats are preferred for such tests, since they clearly indicate small amounts of selenium in the diet by an initial reluctance to eat and by pronounced tissue changes in the liver; thus, the upper lobe was small and atrophied, the one below it being enlarged and thickened, while the surfaces were roughened by prominent lobules which produced a granular appearance. Observations in light from a mercury arc are helpful in this connection, as livers in the anaemic condition associated with the effect of selenium have a blanched appearance. J. G.

Agricultural

***Aspergillus Niger* Method of Examining Soils. A. M. Smith.** (*J. Soc. Chem. Ind.*, 1936, **55**, 217–221T.)—The results obtained for 120 soils by the *Aspergillus* method for estimating the available plant nutrients in soils (Smith and Dryburgh, ANALYST, 1934, **59**, 566) are compared statistically with those found by the Mitscherlich pot-culture method (*cf. Trans. Internat. Soc. Soil Sci.*, 1935, **2**, 95). The correlation-coefficients are +0·72 for the phosphate determination, and +0·53 for the potassium determination. In test experiments 57 per cent. of the soils examined were found by both methods to be definitely deficient in, or well supplied with, phosphorus, whilst for potassium the corresponding figure was only 44 per cent. This conclusion was reached by taking the following limiting values (in mg. per 100 g. of soil) within which the soil may or may not require fertiliser using the *Aspergillus* method, *viz.* below 0·3 or above 0·6 for phosphorus (as P_2O_5),

and below 0·3 or above 0·55 for potassium (as K_2O); in such cases other factors peculiar to the particular soil in question must be taken into account in estimating the fertiliser-requirement. Minor variations in the apparent densities of mineral soil samples are not likely to lead to serious discrepancies in the results obtained in routine tests using the *Aspergillus* method, but, in comparing results, allowance should be made for the fact that in this method (on account of the small quantities required) the soil is weighed out, whilst, in the Mitscherlich method, it is measured by volume. Since the composition of the mycelium is not constant and does not provide a direct measure of the nutrient absorbed by the fungus during growth, figures showing the variation in composition of the mycelium according to its yield are used to calculate the amount of phosphorus or potassium removed from 100 g. of soil at different degrees of development of the organism. The percentage of P_2O_5 increases from 0·3 to 0·7 as the yield of oven-dry mycelium increases from below 0·25 to about 1 g., the corresponding figures for K_2O being 0·25 to 0·67 and 0·25 to about 1 g., respectively. In order to establish the point at which the method shows a response to an application of fertiliser to the soil, the available potassium or phosphorus was determined with and without addition of various quantities of potassium sulphate or ammonium dihydrogen phosphate to the culture solutions. The response to small amounts of phosphorus is feeble, but additions of potassium salt corresponding with a normal dressing of fertiliser effect marked increases in growth. In control experiments it has frequently been observed that the growing fungus develops a cord-like formation instead of the usual felty appearance, and the yield, even in the presence of an excess of potassium and phosphorus, is then always much less than that obtained in the presence of 0·5 g. of infertile soil in the same culture solution; this abnormality has been attributed to the catalytic effect of organic matter, but it is now shown to be due to manganese. Thus, loss of organic matter by ignition or by treatment with hydrogen peroxide produced no significant change in the yield of mycelium, but extraction overnight with 1 per cent. citric acid at 35° C. removed an important constituent in the nutrient requirement of the fungus. It is known that several metals, as well as powdered glass or sand, influence the development of the organism in culture solution (*cf.* Bertrand and Javillier, *Compt. rend.*, 1911, **152**, 226, 900; and Steinberg, *Amer. J. Bot.*, 1919, **6**, 330), and in the present instance addition of 0·0001 to 0·01 per cent. of manganese (as manganese sulphate) had a stimulating effect, which was substantially the same irrespective of the amount added within these limits. However, in the presence of the usual complete culture solution even the most infertile soils yielded over 1 g. of mycelium, and addition of 0·0001 per cent. of manganese effected no significant increases in the potassium and phosphorus values. It is suggested that the method might be adapted to provide a rapid means of estimating a possible deficiency of these minor elements in the soil (*cf.* Mehlich, Truog and Fred, *Soil Sci.*, 1933, **35**, 259). J. G.

Organic

Reagent for Oxidising Agents. P. Pratesi and R. Celeghini. (*Gazz. Chim. Ital.*, 1936, **66**, 365–370.)—The compound, 2.5.*bis* (2.4.dimethyl-N.pyrryl) 3.6.dibromohydroquinone, is a very sensitive indicator for the presence of oxidising

agents, both organic and inorganic, which convert it into the blue quinone. In pyridine solution the hydroquinone can be used for the detection of acyl and alkyl peroxides, and is of more general application than potassium iodide. The intermediate formation of peroxides, and the activation of molecular oxygen in many processes of autoxidation and polymerisation can be established by means of this reagent. The hydroquinone derivative is prepared as previously described (Pratesi, *Gazz. Chim. Ital.*, 1936, **66**, 215) from 2.4.dimethylpyrrole and 2.5.dibromoquinone, the former being obtained by saponification and decarboxylation of 2.4.dimethyl-3.5.carboethoxypyrrole (Fischer and Walach, *Ann.*, 1926, **447**, 41). The dibromoquinone is prepared by brominating hydroquinone and oxidising the dibromohydroquinone with ferric chloride. Twelve g. of dibromoquinone (1 mol.) are suspended in 80 ml. of acetone, treated with 8·6 g. of 2.4.dimethylpyrrole (2 mols.) dissolved in a little acetone, and left for a day; a yield of 8 g. of the hydroquinone is obtained. The reagent, which is stable in air, can be crystallised from a large volume of amyl alcohol. It is very soluble in pyridine, fairly soluble in dioxan and ethyl acetate, sufficiently soluble in ethyl alcohol to give the colour reaction, and practically insoluble in ethyl ether, acetone, chloroform, ligroin, and petroleum spirit. Solutions must be made at ordinary temperatures, as heating leads to the atmospheric oxidation of the hydroquinone derivative, and the solution becomes blue. For the detection of oxidising agents 0·5 to 1 per cent. solutions are used, the oxidant being added alone or dissolved in an inert organic solvent. A blank test should be made. In the presence of an oxidising agent a deep blue colour rapidly develops and the liquid finally becomes opaque; a slight blue colour is also slowly formed in the blank test. Alkali hydroxides and ammonia accelerate the oxidation of the reagent; on the other hand, the reaction is applicable in the presence of hydrochloric or sulphuric acid. E. M. P.

Determination of Nitrate Groups in Carbohydrate Derivatives. J. Dewar and G. W. Brough. (*J. Soc. Chem. Ind.*, 1936, **55**, 207–208T.)—*Materials required.*—(A) Devarda's alloy (powder). (B) Alcoholic potassium hydroxide solution (10 g./400 ml.). (C) Stock sodium hydroxide (approx. 2 *N*). (D) Hydrochloric acid solution (approx. *N*/10). (E) Sodium hydroxide solution (approx. *N*/10). Only the relative titrating values of (D) and (E), and not their absolute concentrations, need be known. *Standardisation of* (*D*).—A weighed sample of pure monoacetylisopropylidenefructose dinitrate (*N* = 7·95 per cent.), in a small glass capsule, was placed in a 250-ml. round-bottomed flask, which was attached to the apparatus for ammonia determinations. From the dropping funnel, 100 ml. of (B) were introduced, the flask was gently shaken, to dissolve the sample, and 50 ml. of (C) were added. The ammonia evolved was absorbed in 10 ml. of (D). After 10 minutes, heat was applied for 30 minutes more. The excess of acid was titrated with (E), and the weight of nitrogen equivalent to 1 ml. of (D) was calculated. *Method of analysis.*—The same method as in standardisation is used, the standard substance being replaced by the one examined; only about 0·1 g. is required. The method is rapid and has given accurate results with a large number of different compounds. If both nitro- and nitrate groups are present, only the nitrogen of the latter is converted into ammonia; this reaction

is quantitative. In test analyses 50 ml. of (C) was insufficient for a tetranitrate, whilst the tendency to froth over was very great with 100 ml. Therefore, 80 ml. were run in, and when nearly all the alcohol had distilled, 20 ml. of water were added carefully; the results were then satisfactory.

The titanous sulphate method, *J. Soc. Chem. Ind.*, 1934, **53**, 236T, is considered unsatisfactory. E. B. D.

Polymerisation of Grape-seed Oil. M. Brambilla and G. Balbi. (*Chim. e Ind.*, 1936, **14**, 353–355.)—Previous work has shown that grape-seed oil polymerises on heating (*cf.* Holde, *Kohlenwasserstofföle und Fette*, Berlin, Springer, 1933, p. 799), and the use of the oil in varnishes has been suggested (Gardner, Paint Mfrs. Assoc. U.S., *Techn. Circ., No.* 190, Oct., 1923; *Chim. et Ind.*, 1924, **11**, 958; Fritz, *Chem.-Ztg.*, 1935, **59**, 704). In the present work the polymerisation of grape-seed oil has been studied with a view to the possible use of such polymerised oils as stand oils in the manufacture of good paints and varnishes. The commercial oil used had the following characteristics: sp.gr. at 15° C., 0·9231; n_D^{20}, 1·4771; viscosity (Engler degrees at 100° C.), 1·57; iodine value, 118; Maumené value, 86·3; acid value, 8·97. It was decolorised with activated charcoal and polymerised at about 330° C. under reduced pressure (about 200 mm.), a stream of pure dry carbon dioxide being bubbled through the oil during the heating. Samples were removed at intervals of 15 minutes, up to 150 minutes' heating, and examined; graphs of the results are reproduced. The specific gravity, refractive index, viscosity, and acid value gradually increased, and the iodine value and the Maumené value decreased during the heating. Continuation of the heating up to eight hours produced a brown, viscous, but not solid product. After 150 minutes' heating products similar to commercial linseed oil were obtained; these should be suitable for clear varnishes and for paints with a white base. After 120 minutes' heating the oil had good drying properties. The acid value of the polymerised oil is high (*e.g.* 34 after 150 minutes' heating), which may make it impossible to use the oil in conjunction with certain pigments, but the acid value of the original oil was also high, and it seems probable that a neutral oil might give a polymer no more acid than analogous linseed oils. E. M. P.

Chloro-Iodo Derivatives of Linolic and Linolenic Acids and Dichloro-diiodo Derivative of Linolenic Acid. Y. Toyama and T. Tsuchiya. (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 219–220B.)—Partial additions of iodine chloride to linolic and linolenic acids were made. Linolic acid was treated with half the theoretical quantity of iodine chloride (1 mol. ICl. for 1 mol. linolic acid) in glacial acetic acid, and the product was fractionally separated by means of methanol containing varying proportions of water. The main fraction was subjected to ozonolysis and, on elimination of the halogens, azelaic and nonylenic acids were obtained. Hence the chloro-iodo-derivative which constitutes the main fraction is 12,13-chloro-iodo-$\Delta^{9:10}$-octadecenoic acid having the following formula: $CH_3.(CH_2)_4CH(ICl)CH.CH_2CH=CH.(CH_2)_7COOH$; this shows that iodine chloride attacks the 12:13 ethylenic linking of linolic acid, leaving the 9:10 ethylenic linking unsaturated. On treating linolenic acid with one-third of the theoretical quantity of iodine chloride in the same way, the main fraction consisted of the

chloro-iodo derivative $C_{18}H_{30}O_2(ICl)$ and, on ozonolysis, acetaldehyde, carbon dioxide and non-volatile compounds resulted. Azelaic and hexenic acids were identified among the acidic products. The chloro-iodo derivative is thus regarded as 15,16-chloro-iodo-$\Delta^{9:10,12:13}$-octadecadienoic acid. On treating linolenic acid with two-thirds of the theoretical quantity of iodine chloride by a similar procedure the dichloro-diiodo derivative was the main product, $C_{18}H_{30}O_2(ICl)_2$, and after ozonolysis azelaic and nonadienoic acids were identified, proving the haloid derivative to be 12,13,15,16-dichloro-diiodo-$\Delta^{9:10}$-octadecenoic acid having the formula $CH_3.CH_2.CH(ICl)CH.CH_2.CH(ICl)CH.CH_2.CH = CH.(CH_2)_7.COOH$; this shows that iodine chloride attacks principally the 15:16 and 12:13 ethylenic linkings of linolenic acid, leaving the 9:10 ethylenic linking unsaturated.

D. G. H.

Wax of *Psylla buxi*. B. K. Blount. (*J. Chem. Soc.*, 1936, 1241–1242.)—*Psylla buxi* flourishes in summer on shoots of box bushes and excretes curved filaments of waxy material. The wax was isolated by extracting a mixture of insects and wax with boiling chloroform, filtering, evaporating to a small volume, adding alcohol and crystallising the brownish wax twice from chloroform-alcohol. Colourless scales with m.p. 89·6°–90·1° C. were obtained. Hydrolysis gave equal amounts of acid and alcohol, the former melting at 92·7° C., and giving an ethyl ester of m.p. 68·8° C. A mean chain-length of 29·9 was deduced, such as would be provided by a mixture of 95 per cent. of the C_{30} acid with 5 per cent. of the C_{28} compound. Such a mixture would have a theoretical m.p. of 93° C. (Piper, Chibnall and Williams, *Biochem. J.*, 1934, **28**, 2175). The alcoholic portion melted at 86·2° C., and yielded an acetate of m.p. 68·7° C. with a mean chain-length again of 29·9, as given by a mixture of 95 per cent. of the C_{30} alcohol and 5 per cent. of the C_{28} compound and melting at 86·2° C. The conclusion is drawn that the wax consists of an ester of equivalent amounts of the C_{30} acid and alcohol, each containing about 5 per cent. of the C_{28} compound. It contains little or no paraffin, thus differing from most insect waxes. D. G. H.

Estimation of Soap by Titration in Petroleum Solvents. T. M. B. Marshall. (*J. Soc. Dyers and Col.*, 1936, **52**, 299–302.)—Additional notes on the experimental procedure are provided (*cf. id.*, 1935, **51**, 241). The 0·1 *N* potassium hydroxide solution is prepared by dissolving 6 to 6·5 g. of the solid alkali in 10 ml. of water, a mixture of 390 ml. of white spirit (b.p. 140° to 180° C., but not otherwise purified), 200 ml. of methylated spirit, and 400 ml. of *n*-butyl alcohol being then added. The 0·1 *N* hydrochloric acid is prepared by dissolving 10 ml. of the conc. acid in a mixture of 400 ml. of *n*-butyl alcohol and 590 ml. of white spirit. The methylated spirit should be purified by shaking it with 1 g. of potassium permanganate and 2 g. of anhydrous soap flakes per litre, the supernatant liquid obtained after standing for 24 hours being distilled over quicklime or potassium carbonate; portions of the distillate which turn brown after being boiled for a few minutes with a strong solution of potassium hydroxide and standing for 15 minutes should be rejected (yield 75 per cent.). The butyl alcohol is purified by heating the "technical" alcohol under a reflux condenser with 2 g. per litre of potassium

hydroxide for 30 minutes, and collecting the fraction having a b.p. of 114° to 117° C. (yield 80 per cent.). The alkali may be standardised preferably by titration with a standard solution of pure oxalic acid in methylated spirit, with phenolphthalein as indicator. The acid is standardised either against the alkali, or by titrating with it a mixture of 25 ml. of neutral methylated spirit with a solution of x (*e.g.* 0·2 to 0·3) g. of pure dry mercuric oxide in 10 ml. of 10 per cent. potassium iodide solution; then the normality factor for the 0·1 N acid is given by $x/0{\cdot}0108 \times$ volume of acid required to neutralise the potassium hydroxide liberated, using phenolphthalein as indicator. The "soap indicator" used in the determination is a solution of 0·16 g. of eosin and 0·04 g. of xylene cyanol-*FF* in 100 ml. of a mixture of equal volumes of methylated spirit and *n*-butyl alcohol. Its *p*H range was studied by means of a series of buffer solutions made up in water, and the colour was found to be red with a green fluorescence down to about *p*H 5·0, below which it passed through dull magenta (green fluorescence), and at about *p*H 3·6 became blue-green and non-fluorescent, then green at *p*H 2·0, and finally yellow in strongly acid solutions. It is sensitive to acids having a dissociation-constant above 1×10^{-4} and to caustic alkalis and alkali carbonates, but not to carbonic acid or the weaker organic acids. The actual method has also been reviewed and the following procedure is recommended:—Phenolphthalein is added to a solution of 0·5 to 1·0 g. of soap in 25 ml. of a mixture of equal volumes of methylated spirit and *n*-butyl alcohol (warmed if necessary), and the mixture is titrated with the standardised acid or alkali (*supra*) in order to obtain the amount of alkali or free fatty acids present, respectively. The soap indicator is then added to the neutralised solution, which is titrated with the standard acid until the fluorescent red colour is replaced by a non-fluorescent blue-green shade (*p*H 3·6 to 3·8), this titration giving the amount of combined alkali. If the nature of the fatty acid is known, the amount of soap present may then be calculated. When dry-cleaning soaps containing free fatty acid were titrated with alkali to phenolphthalein and then back-titrated with acid, with the use of the soap indicator, a difference between the end-points was noticed, the average value of this difference being about 1 ml., although this figure was too variable to be used as a correction. It was also found that organic acidity in the methylated spirit or butyl alcohol used in the standard solutions produced similar differences, which increased with an increase in the period of storage of a solution of a strong alkali in mixtures of these solvents, whether they contained white spirit or otherwise. These differences are attributed to the production of acidity which is at once neutralised by the alkali, so that the reaction tends to proceed towards completion. Carbonate impurities in the alkali also produced a difference in end-point, because the phenolphthalein measures only one-half of the carbonate, whilst the soap indicator shows all the alkali present. There is little difference in the end-points if the solvents are purified as described above. Determinations of the percentage of total alkali (as Na_2O) are recorded for 20 soaps of various kinds (bar- and flake-types); there is good agreement between results obtained by the above method and by ashing a weighed quantity of soap and titrating with a standard solution of acid in water, and the method is recommended for rapid routine analysis.

J. G.

Effect of Heat, Gasoline, and Methanol on the Solubility of Sesame Seed Protein in Salt and Alkalis. W. H. Adolph and I. Lin. (*Ind. Eng. Chem.*, 1936, **28**, 734–735.)—Sesame seed contains about 22 per cent. of protein, mainly globulin, which resembles "vegetable casein" and may be used as a plastic and adhesive. Ground seed, from which the oil had been extracted with ether, was treated as follows:—(*a*) Forty g. were kept at 110° C. for 3 hours. (*b*) Forty g. in 100 ml. of commercial gasoline (b.p. 85° C.) were kept at 60° C. for 3 hours; the gasoline was then evaporated. (*c*) As for (*b*), with the substitution of methanol for gasoline. The solubility of the material in solutions of sodium chloride, sodium hydroxide, and sodium carbonate was found to be little influenced by treatment (*a*) or (*b*). After treatment (*c*), solubility in sodium hydroxide was decreased slightly, more in sodium carbonate solution, and very greatly in sodium chloride solution. The results are shown graphically, the concentration of the alkalis being given as *p*H values. *Method of determination.*—One-gram samples were shaken with 50 ml. of solvent for 3 hours at 25° C. After filtration, the nitrogen was determined on 25 ml. of filtrate. Optimum yields on re-precipitation were obtained from solutions in $N/50$ sodium hydroxide, by (*a*) adding 6 N sulphuric, hydrochloric, or acetic acid to give a *p*H of 4·8, or (*b*) heating to 60° C. The coagulated protein was separated by filtration on cloth and air-dried, and the nitrogen was determined. The protein yield, calculated to an ash- and moisture-free basis in terms of the original protein, averaged (*a*) 51·8 per cent. (nitrogen-content, 15·1 per cent.), and (*b*) 43·8 per cent. (nitrogen-content, 15·0 per cent.). E. B. D.

Report of the Committee on Specifications for Standard Tannin Dishes. J. S. Rogers (*J. Amer. Leather Chem. Assoc.*, 1936, **31**, 300–302.)—The following specification has been adopted: The dish shall be of non-soluble glass, with an over-all height of 50 mm. and an outside diameter of 70 mm. The top edge shall be well rounded and thoroughly fired to minimise chipping in service; the bottom corner to be well rounded, conforming to a 6-mm. radius; the bottom is to be flat, not cupped in the centre, thus avoiding localisation of residue films and unsatisfactory drying. The weight of the dish is to be 30 to 39 g., a narrow weight range eliminating much changing of weights during drying and making possible more rapid and accurate weighing of tannin residues.

E. M. P.

Inorganic

Detection of Silver and Mercury. N. A. Tananaeff. (*Z. anal. Chem.*, 1936, **106**, 167–170.)—The reaction is an induced reduction of mercuric chloride to metal by stannous chloride in presence of a silver compound. The unknown solution, which may contain an indefinite number of elements, is treated with a few drops of silver nitrate and stannous chloride solutions. If the solution contains mercuric salt, an intense black turbidity or precipitate is obtained; if the solution contains silver besides mercuric salt, the formation of the black precipitate proves the presence of both. The reaction can be used as a spot-test on filter-paper. To a drop of stannous chloride is added a drop of silver nitrate solution and one

of the liquid to be tested; a black coloration is given by mercuric salts. For the detection of silver, a drop of the unknown solution is added to one of mercuric nitrate solution, followed by a few drops of stannous chloride. W. R. S.

Rapid Method for the Determination of Copper. L. Jolson. (*Z. anal. Chem.*, 1936, **106**, 157–167.)—The method consists in the precipitation of copper as acetylide and titration of the red suspension with cyanide until decolorised. The solution, containing 0·025 to 0·05 g. of copper and not more than 2 g. of ammonium salts, is treated with 10 ml. of strong ammonia, 0·1 g. of hydrazine or hydroxylamine hydrochloride or sulphate, and 25 ml. of a 0·1 per cent. gelatin solution, and the mixture is diluted to 100 ml. with hot distilled water. When the solution is colourless, a stream of acetylene is passed for a minute, after which the solution is titrated with one containing 1 to 10 g. of potassium or sodium cyanide per litre, during constant agitation until colourless. If iron or zinc is present, a solution of 5 g. of sodium pyrophosphate should also be added to the copper solution. The cyanide solution is standardised against copper nitrate solution (1 g. Cu in 1000 ml.). In presence of iron and zinc, standardisation should be effected after addition of equivalent quantities of these metals. An accuracy of ±2 per cent. is attained, the process occupying 5 to 6 minutes. A description is given of the method as applied to sulphide ores, flotation tailings, and slags. W. R. S.

Determination of Silver Halides in Photographic Materials. S. Whiteley and O. V. Soane. (*J. Soc. Chem. Ind.*, 1936, **55**, 167T.)—Silver halides are determined by a modification of Clark's electrometric method, using an electrometer valve potentiometer (Morton and Best, *J. Soc. Chem. Ind.*, 1923, **52**, 6T). The determination is complete in 1 to 1½ hours. *Method.*—Thirty to 40 sq. in. of negative material, 80 sq. in. of bromide paper, or 80 to 120 sq. in. of chlorobromide and gaslight papers, are the minima required. The material is "fixed" in a developing dish with 50 ml. of potassium cyanide (approximately $N/5$), the halide solution is poured off into a 500-ml. conical flask and diluted with about 100 ml. of water, 2 to 3 g. of zinc dust are added, and the solution is heated to the boiling-point slowly to diminish frothing. It is boiled for 15 minutes, 20 ml. of glacial acetic acid are added, and the solution is boiled again for 5 minutes, to drive off hydrogen cyanide, and filtered into a 250-ml. beaker. The silver electrode dips into the solution and the saturated calomel electrode into 3 N ammonium nitrate solution; the two solutions are connected by a salt bridge containing 3 N ammonium nitrate solution. If iodide is present, the silver electrode is connected with the valve terminal of the potentiometer and the calomel electrode with the other terminal. After the iodide end-point has been passed the connections are reversed. To prevent formation of mixed silver halide crystals or adsorption phenomena, 2 to 3 g. of potash alum are added to the halide solution. The solution is titrated by running in $N/20$ silver nitrate solution slowly to determine the iodide, after which $N/10$ silver nitrate solution is used for the bromide and chloride determinations. Near the end-points, additions are made of 0·05 ml. at a time, the reading in millivolts being taken after each addition. Near the iodide end-point 1 to 1½ minutes elapse before equilibrium is reached

after each addition. The end-points are those where the rate of change of potential is a maximum. This method gives the relative amounts of the different halides present. The amounts per unit area can be determined by using an aliquot portion of an accurately measured cyanide solution. *Remarks.*—A water-turbine is preferable to an electric motor for operating the stirrer, as it does not disturb the valve of the meter. If, in chloride and bromide mixtures, the proportion of bromide is less than 5 per cent., a known volume of $N/10$ bromide solution should be added to prevent inaccurate results, while the addition of a known amount of potassium iodide solution to chloride-bromide mixtures makes the bromide end-point sharper. With chloride solutions a blank test on the reagents is necessary. The silver electrode, which is a silver plate, about 4 cm. × 1·5 cm. × 0·15 cm., fused to a silver wire, should be cleaned after about six determinations, preferably with metal polish. Duplicate analyses of commercial films and papers were satisfactory, but emulsions coated on glass plates gave the following results:

	Present Per Cent.	Found Per Cent.
Silver iodide ..	6·3	6·1
,, ,, ..	2·1	2·1
Silver bromide ..	62·0	61·3
,, ,, ..	15·0	14·9

The differences may be due to the difficulty of calculating the proportions of halides present in a gelatin emulsion. The results would include soluble halide, if present in the emulsion, but the amount of this should be relatively small.

E. B. D.

Specific Bismuth Reaction. N. A. Tananaeff. (*Z. anal. Chem.*, 1936, **105**, 419–422.)—The reaction is based upon the reducing properties of potassium manganocyanide. A half-saturated potassium cyanide solution is treated with a 10 per cent. solution of a manganous salt until the dark green precipitate re-dissolves with difficulty, 5 to 10 seconds being required for its disappearance. The reagent should be freshly prepared. The liquid to be tested, which should contain 10 per cent. of free hydrochloric or nitric acid, is slowly poured into a test-tube containing the reagent and held in an inclined position. If bismuth is present, a black ring is formed at the zone of contact of the two layers, due, according to the author's tests, to the precipitation of bismuth monoxide. No other metals interfere with the test.

W. R. S.

Separation of Bismuth from Lead and Copper. E. A. Ostroumow. (*Z. anal. Chem.*, 1936, **106**, 36–45.)—The bromate-bromide method of Moser and Maxymowicz (Abst., ANALYST, 1926, **51**, 161) was found to effect an accurate separation of bismuth from lead and copper. A modified cyanide procedure for the separation of bismuth from much copper was worked out and found to be reliable. The solution is treated with tartaric or citric acid, neutralised with ammonia, and decolorised with cyanide solution. The bismuth is then precipitated with hydrogen or sodium sulphide, the solution being left on a steam-bath until flocculation has set in. The precipitate is collected, washed twice with dilute cyanide and sulphide solution, and finally with hydrogen-sulphide water.

W. R. S.

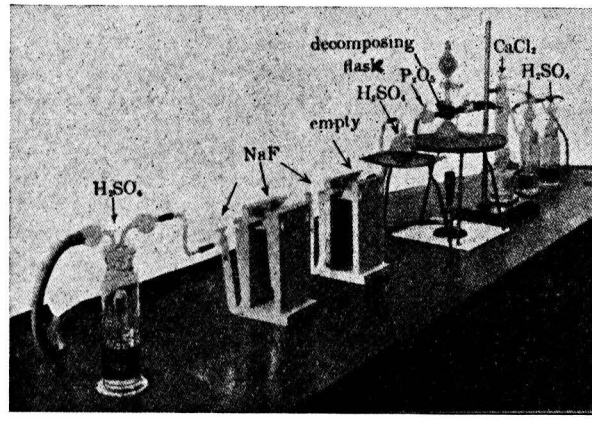
Separation of Tin from Arsenic and Antimony by Means of Cupferron. N. J. Tscherwiakow and E. A. Ostroumow. (*Ann. Chim. anal.*, 1936, **18**, 201–207.)—The solution of the sulpho-salts of arsenic, antimony and tin obtained after the sulphide separation of copper, etc., is acidified with acetic acid, and the precipitation of the sulphides of arsenic, antimony and tin is completed by passing in hydrogen sulphide. The mixed sulphides are filtered off, washed with hydrogen sulphide water, and dissolved in dilute sodium hydroxide solution. The solution is oxidised with hydrogen peroxide and boiled for 15 minutes to destroy the excess of the reagent. It is then acidified with hydrochloric acid, 8 ml. of the concentrated acid (sp.gr. 1·19) being added in excess for each 100 ml. of solution. The solution (not more than 150 ml.) is cooled to 5° C., and an excess of cupferron solution (also cooled to 5° C.) is added with vigorous stirring, which is continued for two or three minutes. This precipitates the tin-cupferron compound in a flocculent form, and good cooling is essential to prevent the precipitate resinifying, when it is difficult to wash thoroughly. The precipitate is filtered off and washed until free from chloride with a well-cooled 0·5 per cent. solution of cupferron. Initial washing by decantation of the bulk of the precipitate is advised. The first portions of the filtrate are sometimes turbid, and are re-filtered if necessary. The paper and precipitate are first dried at about 60° C., and then ashed, and the residue of stannic oxide is ignited and weighed. Arsenic and antimony may be recovered from the filtrate by precipitation with hydrogen sulphide in the usual way. Quantitative results were obtained in tests with 0·03 to 0·003 g. of tin in the presence of up to 0·08 g. of arsenic and 0·06 g. of antimony. Stannous tin is stated also to be quantitatively precipitated by cupferron. Tervalent and quinquevalent arsenic and quinquevalent antimony are not precipitated. Previous methods in which cupferron is employed to precipitate tin were found to be less satisfactory. Pinkus and Claessens (*Bull. Soc. Chim. Belg.*, 1927, **31**, 414) employed only a very slight excess of cupferron, and the precipitation was incomplete with the smaller amounts of tin. It is essential to stir well and add sufficient cupferron to produce a flocculent precipitate. In Furman's method (Abst., ANALYST, 1923, **48**, 626) resinification of the precipitate occurs, owing to insufficient cooling. S. G. C.

Determination of Small Quantities of Iron with the Use of a Silver Reductor. C. F. Fryling and F. V. Tooley. (*J. Amer. Chem. Soc.*, 1936, **58**, 826–831.)—The method of Walden, Hammett and Edmonds (*id.*, 1934, **56**, 350), which involves reduction of ferric chloride in dilute hydrochloric acid solution by passage over metallic silver, followed by titration with standard ceric sulphate solution with the *o*-phenanthroline-ferrous complex as indicator, has been adapted to the determination of amounts of iron of the order of 1·5 mg. A difficulty was met with in the formation of hydrogen peroxide when the solution containing dissolved air passed through the silver reductor, causing apparently incomplete reduction of the ferric iron. This effect, whilst minimised by performing the reduction in an atmosphere of hydrogen by the use of a reductor of special design, still necessitated a correction factor; this was variable and had to be determined at the time of each determination. A further correction is required for the amount of ceric sulphate required to colour the indicator. For working details the paper

should be consulted. The method was applied to the analysis of glass-sand, the iron being determined after removal of silica from a 2-g. sample by heating with hydrofluoric-sulphuric acid mixture. S. G. C.

Separation of Iron, Aluminium and Chromium from Manganese, Nickel and Cobalt by means of Pyridine. E. A. Ostroumow. (*Z. anal. Chem.*, 1936, **106**, 170–176.)—The boiling chloride solution, containing about 0·1 g. of sesquioxides per 100 ml. and ammonium chloride, is treated with an excess of 10 to 15 ml. of 20 per cent. pyridine solution, again boiled, and left on a steam-bath until the precipitate has settled; it is collected and washed with hot water containing pyridine. In presence of 3 g. of ammonium chloride, the amount of adsorbed bivalent metal was found to be less than 0·1 mg., hence a single precipitation suffices. A nitrate solution and ammonium nitrate may also be used. Zinc is partly co-precipitated with the sesquioxides by pyridine. Large amounts of sulphate (*e.g.* after bisulphate fusion) cause formation of basic sulphates of the sesquioxides, with risk of incomplete precipitation and poor filtration. Pyridine impedes the precipitation of nickel dimethylglyoxime; if nickel is to be determined by that reagent, the solution should first be boiled with soda (*sic*) until the pyridine is expelled. The precipitates produced by pyridine filter well and are easily washed. W. R. S.

New Method for Determination of Fluorine. S. Shinkai. (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 162B.)—Numerous fluorides are decomposed when acted on by concentrated sulphuric acid and silica, the fluorine being liberated as silicon tetrafluoride. The novelty of the proposed method consists in absorbing the product in powdered sodium fluoride, with which it reacts according to the equation: $2NaF + SiF_4 = Na_2SiF_6$, and determining fluorine gravimetrically from the increase in weight of sodium fluoride absorption tubes. The apparatus is shown in the figure, but the author gives no working details. Presumably the



silicon tetrafluoride is carried over in a stream of air, it being necessary to avoid admission of moisture; three sodium fluoride absorbing tubes are used. Concordant results of determinations of fluorine in calcium fluoride by this method are cited. S. G. C.

Titration of Iodide in Presence of Bromide and Chloride. A. Mutschin. (*Z. anal. Chem.*, 1936, **106**, 1–11.)—The iodate method for the determination of iodide, antimony, arsenic, etc., was re-investigated. It was found that iodide can be accurately titrated with iodate in presence of bromide if the solution is practically saturated with potassium bromide, which counteracts the dissociation of iodine bromide. Chloride also may be present without affecting the course of the reaction. The salt to be analysed, containing not more than 0·2 to 0·3 g. of potassium iodide or its equivalent, is dissolved in a minimum of water, and treated with 40 ml. of saturated potassium bromide solution, 20 to 30 ml. of strong hydrochloric acid, and just enough water to dissolve the separated crystals, or to dissolve them while the titration proceeds. After addition of chloroform (5 ml.), the solution is titrated with 0·025 *M* iodate solution until the chloroform is colourless. Titration in a graduated 250-ml. flask with a well-fitting stopper is desirable, as the colour of the chloroform layer can be observed in the neck of the inverted flask. W. R. S.

Determination of Chlorate, Nitrate and Persulphate by Means of Vanadous Sulphate. P. C. Banerjee. (*J. Indian Chem. Soc.*, 1936, **13**, 301–304.)—Vanadous sulphate reagent (approximately 0·2 *N*), the preparation of which has been previously described (Abst., ANALYST, 1935, **60**, 573), was standardised by titration with 0·1 *N* potassium permanganate solution. In the following reactions an atmosphere of carbon dioxide was maintained. *Chlorate.*—Reduction to chloride is complete on boiling with the reagent. The chlorate solution was acidified with sulphuric acid, a measured excess of the vanadous sulphate reagent was added, and the mixture was boiled for 5 minutes. The solution was cooled, and the excess of vanadous sulphate was determined by titration with 0·1 *N* permanganate solution (1 ml. of 0·1 *N* vanadous sulphate solution ≡ 0·001775 g. of sodium chlorate). Tests with 10 to 25 ml. of sodium chlorate solution (0·0023 g. per ml.) gave results accurate to within a few tenths of one per cent. *Nitrate.*—Nitric acid is reduced to ammonia on boiling with vanadous sulphate. To a known volume of the vanadous sulphate solution were added 2 ml. of conc. sulphuric acid diluted with 25 ml. of water, followed by the potassium nitrate solution under test. The mixture was boiled for 5 minutes, cooled, and titrated with permanganate solution (1 ml. of 0·1 *N* vanadous sulphate solution ≡ 0·001264 g. of potassium nitrate). Results with 5 to 15 ml. of potassium nitrate solution (0·0012 g. per ml.) were a few tenths of one per cent. below the theoretical. *Persulphate.*—Persulphuric acid is not completely reduced by vanadous sulphate either in the cold or when hot. Tests showed that in the presence of a little ferric salt, the per-acid is completely reduced to sulphate by an excess of vanadous sulphate, even at the ordinary temperature. To a solution of ammonium persulphate were added a few ml. of ferric alum solution (approximately 0·1 *N*), and an excess of vanadous sulphate reagent; the mixture was acidified with sulphuric acid, kept for 2 to 3 minutes, and titrated with permanganate solution (1 ml. of 0·1 *N* vanadous sulphate solution ≡ 0·01141 g. of ammonium persulphate). With 10 to 25 ml. of ammonium persulphate solution taken (0·1 g. per ml.), the results were a few tenths of one per cent. below the theoretical. S. G. C.

Occurrence of Phosphorus in Fusain. A. H. Edwards and J. H. Jones. (*J. Soc. Chem. Ind.*, 1936, **55**, 186–189T.)—Since coal required for production of metallurgical coke for the manufacture of pig-iron is sold subject to a specification that the phosphorus must not exceed a stipulated figure, usually of the order 0·008 per cent., the presence, in the seam, of fusains, which may contain large proportions of phosphorus, becomes of great importance. Fusains, classified as "shaly," blue and soft-black, found in the Brockwell seam in north-west Durham were examined in detail, and, after being crushed to pass a 72 B.S.I. sieve, were subjected to float and sink treatment with carbon tetrachloride. Nearly 70 per cent. of the "shaly" fusain had a sp.gr. greater than 1·6, with an ash-content of approximately 50 per cent., and a phosphorus-content of over 8 per cent. The "floats" had an ash of over 10 per cent., with a phosphorus-content over 15·0 per cent. Photomicrographs indicate the term "shaly" to be a misnomer, as the substance was a normal fusain with the cells completely filled with mineral matter. Blue fusain yielded nearly 90 per cent. of "floats" with an ash of 2·8 per cent. and an abnormally high content of phosphorus, and the soft black fusain, although giving an exceptionally low figure for ash, still had a high phosphorus-content. A "shaly" fusain from the Brockwell seam yielded a total ash of 33·4 per cent. containing the following constituents:—SiO_2, 2·14; Fe_2O_3, 8·35; $Al_2O_3 + TiO_2$, 5·72; CaO, 49·65; MgO, 3·67; K_2O, 0·14; Na_2O, 0·33; SO_3, 0·82; P_2O_5, 29·61; total, 100·43 per cent. The fusains examined, although abnormal, were fairly widespread, and an analysis of selected samples from six different seams showed a range of phosphorus in the ash from 0·03 to 0·8 per cent., with one sample containing 4·54 per cent. This last occurred as a ½-inch parting in a 34-inch seam. The presence in a seam, otherwise complying with the phosphorus limit, of, say 0·3 per cent. of material similar to a "shaly" fusain, such as one of those examined, would treble the phosphorus-content. Fusains with abnormally high phosphorus-content have also been found in Yorkshire, and a survey of German fusains showed some with high phosphorus-content. D. G. H.

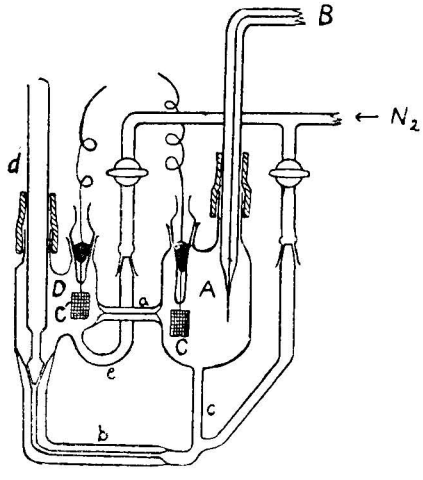
Microchemical

Collected References. Mikro-balances. G. Gorbach. (*Mikrochem.*, 1936, **20**, 254–337.)—A detailed account is given of different types and makes of micro-balance and various problems in connection with their construction and use. Under the heading "Constancy of the Balance" various devices for maintaining a constant temperature are described, including the use of dur-aluminium for the construction of the floor and the back of the balance-case. The rider-error of the Kuhlmann type of balance is described; this may be large, since not only is the position of the rider at the exact bottom of the groove in the rider scale essential, but it must also be vertical, as a deviation of only 1° from the vertical is stated to be capable of causing a weight-difference of 6γ. To remedy this, a special "stick rider," consisting of a cylindrical stick of quartz weighing 2 mg., has been invented. This requires a special rider-attachment for placing it in position (Sartorius balance with Ramberg rider-attachment). To simplify and accelerate

reading of the microscope, damping devices are now used. Air damping is preferable to oil or magnetic damping. Many modern micro-balances have a projection device for reading the pointer scale, which is less tiring than the direct method. Various models of the Pregl type of balance are illustrated—the Kuhlmann balance with mirror reading, and with microscope reading, the corresponding Bunge models, the Starke and Kammerer balance, the Sartorius balance with microscope reading, and with special rider-beam cover and illumination from behind, and also the type with the Ramberg stick-rider and microscope reading; the Nemetz balance, and the Kaiser and Sievers balance with projection reading. The aperiodic type of balance is described in detail, with illustrations of the Kuhlmann (brake-damping) and Bunge, Sartorius, and Kaiser and Sievers air-damped models. The semi-micro balances of Bunge and Sartorius are illustrated and described. Other types of micro-balance described include (i) the Steele and Grant (vacuum-balances), (ii) Nernst type (torsion-balance) (iii) spring-and-torsion balances, of which the Hartmann and Braun torsion-spring balance for rapid weighing is the one most frequently used, (iv) various kinds of electromagnetic balances. The summary contains 90 references. J. W. M.

Microchemical References in 1935. (Appendix to *Mikrochem.*, 1936, **20.**) Seventy-two pages of references to publications on microchemical subjects listed in alphabetical order of the authors' names under the following headings:—I, *Pure Microchemistry*: (i) General and apparatus; (ii) Inorganic analysis; (iii) Organic analysis; (iv) Preparative chemistry; (v) Physical chemistry. II, *Applied Microchemistry*: (i) Biological chemistry; (ii) Medical and pharmaceutical chemistry; (iii) Mineralogical chemistry; (iv) Technical chemistry. J. W. M.

Determination of Traces of Ferric Iron. J. Dubnoff and P. L. Kirk. (*Mikrochem.*, 1936, **19**, 194–207.)—A differential electrometric titration method, using titanous chloride, is adapted for the determination of 2 to 5γ of iron such as is present in a few ml. of serum. *Reagents.*—(i) Stock solutions of ferric salts, 0·001 *N*, were made by various procedures and checked against each other. (ii) Dilute ferric iron standards: each day solution (i) is diluted with 0·5 per cent. hydrochloric acid to exactly 0·00002 *N* for standardisation of titanous chloride. (iii) Titanous chloride solution: 20 per cent. titanous chloride solution diluted with 0·5 per cent. boiled hydrochloric acid to 0·001 *N* in an evacuated bottle and kept protected from the air. This will keep for several days. (iv) Potassium thiocyanate solution: 10 per cent. (v) Trichloroacetic acid solution: 10 per cent. *Apparatus.*—(*a*) A differential titration vessel (shown in the diagram) of about 5-ml. capacity, consisting of reaction chamber A and retarded chamber D, each containing a



bright platinum electrode C and C′, connected with a galvanometer of sensitivity 25 millivolts per mm. through a tapping key and variable resistance. A flow of nitrogen through the vessel ensures a steady galvanometer reading, and the flow is regulated by means of a MacInnes and Dale gas lift pump (*J. Amer. Chem. Soc.*, 1929, **51**, 1119) c; flow of solution through c is controlled by the ground plunger, *d*. (*b*) A capillary burette with mercury screw tap; and (*c*) a nitrogen-purifying train consisting of a quartz tube containing reduced copper heated to 700°–750° C., connected with a cylinder of nitrogen. *Method.*—A sample of not more than 5 ml. is placed in the titration vessel and acidified (not more than 1 *N*) with hydrochloric acid; the electrodes should be covered. The titration vessel is attached to the burette, and the nitrogen is allowed to flow. On lifting the plunger at the bottom of the retarded chamber the solution in both chambers mixes. After half-an-hour the plunger is lowered and titanous chloride is added until the galvanometer deflection shows a rapid increase. The solution is then mixed again, and titanous chloride is added in small equal increments, with mixing after each addition. The number of increments is plotted against the galvanometer deflection, the burette reading at the sharp peak was taken, and from this 0·5 of an increment was subtracted to give the correct end-point in the experimental conditions. The correction was found to be right both in theory and practice. A large number of determinations on standard solutions gave a maximum deviation of 2 per cent. from the mean. The addition of thiocyanate causes a decrease in titre, probably owing to a reducing action on ferric iron; this action increases with the time of mixing and of sweeping out with nitrogen, and after half-an-hour the loss may be 20 per cent. Therefore thiocyanate is not added except in the determination of iron in the trichloroacetic acid filtrate of blood serum, when it appears to be essential. In that case the titanous chloride is standardised against iron, the same amount of thiocyanate being used; the results showed a maximum deviation of 3 per cent. from the mean.

J. W. M.

Measurement of Geologic Time by Means of the Micro-analysis of Radioactive Minerals. F. Hecht and E. Kroupa. (*Z. anal. Chem.*, 1936, **106**, 82–103.)—The "lead method," one of the most exact means for the measurement of geologic time, is based on the disintegration of uranium and thorium, and consists in determining the two elements as well as the lead isotopes RaG and ThD in minerals other than secondary ones, especially such as have not undergone alteration by weathering. The study of the products of weathering may, however, also furnish certain clues. The detection of differences in layers parallel to the crystal surface also is of importance, as it has been found that enrichment in lead has sometimes taken place in the outer zone. In analyses of this kind, micro- or semimicro-methods are necessary on account of the small amount of material available or the very low percentages of lead and radioactive metals present. It is assumed that atomic disintegration proceeds uniformly throughout time. The ratio of lead to uranium or thorium, or both, is termed the "lead ratio," from which the age is calculated according to the formula—

$$\text{Age in year-millions} = \frac{\text{Pb}}{\text{U} + k.\text{Th}} C$$

C is a factor depending on the atomic weight of the radio-lead in the mineral (206 to 208), and its variability is therefore rather small; it closely approximates 7100. The factor k has a more uncertain value; it represents the ratio between the disintegration constants of thorium and uranium, and is required because thorium disintegrates more slowly than uranium, but the constant of thorium is not so well known as that of uranium. Some investigators use $k = 0{\cdot}25$, others prefer 0·36 to 0·38. The uncertainty due to this factor is, of course, confined to thorium-bearing minerals. The percentage of lead used for the calculation must not include ordinary lead, the presence or absence of which should be proved by an atomic weight determination. In practice, the measurement of geologic time is concerned less with the determination of an absolute scale in year-millions than with the allocation of a definite lead ratio to a particular geologic epoch. Such a scale is not based altogether on theoretical considerations: it can be correlated with the relative age as determined by the identification of characteristic fossils. The whole subject is as yet in an early stage.

Numerous micro- and semimicro-analyses are reproduced in the paper. The minerals listed are uraninite, pitchblende, thorianite, monazite, allanite, and Swedish kolm ash (oil shale from the upper Cambrian, carrying trilobites). A selection of some results and their interpretation are given below.

Mineral	Lead ratio	Age (year-millions)	Geologic epoch
Pitchblende, Great Bear Lake ..	0·193	1320	Laurentian
Uraninite, Frederikshald	0·159	1250	Do.
Allanite, Amherst Co., Virginia ..	0·111	800	Pre-Cambrian
Kolm ash, Sweden	0·0574	425	Cambrian
Uraninite, Fitchburg, Mass. ..	0·0492	360	Early Silurian
Do. Portland, Conn. ..	0·042–0·046	280–290	Late Devonian
Do. Jim Claim, Canada ..	0·0115	80	Eocene

W. R. S.

New Principle in the Absorption of Gases. Determination of Small Amounts of Volatile Bromides. F. L. Hahn. (*Mikrochem.*, 1936, **20**, 239–246.)—A constituent present in small quantities in a gas mixture may, in some instances, be separated by admixing the vapour of an easily condensable solvent for that constituent and cooling, the condensed solvent then carrying down with it the required constituent in solution. The principle is applied to the determination of small amounts of ethyl bromide in physiological material. The alkyl halide is driven off from the heater material and conveyed in a stream of air to mix with a little water vapour before being passed through a red-hot quartz tube. The separated bromine forms hydrogen bromide, and this, when passed through a condenser, is taken up by the condensed water, and can then be determined colorimetrically by the author's method (*Mikrochem.*, 1935, **17**, 222). The apparatus is made entirely of glass and quartz with ground-glass joints. The substance to be examined is heated in a small vertical hard glass tube, the inlet and exit for air passing through the cap, which fits over the tube with a ground-glass joint and glass hooks for clips. The water for the steam enters through a small tap funnel joined by means of a side arm to the exit tube from the heated tube.

The gases pass horizontally through the hot quartz tube, and the condenser is vertical. The time required for the complete evolution and collection of 90γ of ethyl bromide is 40 minutes, and the volume of water condensed is about 0·5 ml. per minute. J. W. M.

Physical Methods, Apparatus, etc.

Determination of the Melting-point of Coal Ash. H. A. J. Pieters. (*Chem. Weekblad*, 1936, **33**, 519–520.)—The ash is ground well and made into a thick paste with water, and this is partly dried and placed in a hollow brass mould so as to fill it completely. The mould is a truncated pyramid, each of the 3 sides of which is 6 mm. wide at the base and 2 mm. at the top, and 25 mm. high. The mould and its contents are dried for a few minutes at 80° to 100° C., after which the moulded sample may be removed whole; it is then fixed by means of china-clay paste to a flat plate, which is inserted in an oven not more than 5 mm. from the end of a thermo-couple inserted so that its extremity is in the middle of the oven. The oven (length 200 mm., internal width 60 mm., external width 150 mm.), has a hinged lid, and is heated electrically by means of 4 carborundum elements carrying a current of 5 to 6 amps; hydrogen is passed through it at the rate of 45 litres per hour, a wash-bottle and manometer being provided on the inlet side to assist control of the volume. The temperature, which should not exceed 800° C. initially, is raised by adjusting the resistance, first at the rate of 10° to 15° C. per minute, and in the neighbourhood of the m.p., at about 3° C. per minute. The m.p. is reached when the top of the pyramid bends over and touches the base. An illustration of the apparatus is provided. J. G.

Reviews

MOLYBDENUM STEELS: THEIR MANUFACTURE AND APPLICATION. By JULIUS L. D. VOGEL, M.I.E.E., M.I.M.M., and W. F. ROWDEN. Pp. 103. London: High Speed Steel Alloys, Ltd. Price 5s.

The authors, who are members of the technical staff of High Speed Steel Alloys, Ltd., and consequently in close touch with the manufacture and practical application of special steels, have produced a well-balanced and authoritative account of the distinctive characteristics conferred by the presence of molybdenum in carbon and alloy steels. The rapid increase in the output of molybdenum steels in the last ten years is largely due to the fact that the addition of a fraction of one per cent. of molybdenum not only improves the mechanical properties of steel at ordinary and at raised temperatures, but also reduces "mass effect" and eliminates temper brittleness. In other words, it promotes effective hardening in very large masses of alloy steels and permits of slow cooling from the tempering temperature without detriment to the shock-resisting properties of the steel. These advantages are not secured without special attention to certain features in manufacture and treatment, and the authors are careful to point out just where additional precautions are necessary in the presence of molybdenum.

The commercial products employed for the introduction of molybdenum into steel are dealt with, and methods of analysis of molybdenum products are given. The methods, which are briefly but adequately described, call for little comment, except that it would seem preferable invariably to convert the separated molybdenum into lead molybdate and weigh it as such rather than to weigh it as the sulphide or oxide.

The book is a careful and trustworthy record of the properties of molybdenum steels, and contains many good photographs illustrating their commercial applications. B. S. EVANS

PRACTICAL MANAGEMENT OF PURE YEAST. By ALFRED JÖRGENSEN. Third Edition, revised by ALBERT HANSEN. Pp. xii + 111. London: Charles Griffin & Co., Ltd. 1936. Price 6s. net.

Scientific workers in the fermentation industries are already acquainted with the previous editions of this book, published in England for the first time in 1903; the second edition, published in 1913, was reviewed in the *Journal of the Institute of Brewing*, 1913, p. 515.

The book is primarily intended for students of brewing and allied industries, in which the use of pure culture yeasts is desirable, and is purely practical in its aims. The text is divided into two parts, the first dealing with the biological analysis of yeast in breweries, distilleries and yeast factories and, less fully, with wine yeast. The biological analysis of air and water receives some attention, and a section is devoted to the preparation of nutritive media. The second part deals with the preparation of pure cultures, methods of increment and their use in practice. Degeneration of yeast is discussed, and some space is given to methods of preservation of cultures.

Important additions to the text include a summary of the classification of the yeasts and a description of Schlesinger's method for the biological examination of water by determining its so-called destructive power which represents an arbitrary product of time and dilution factors, determined experimentally by inoculating the water in decreasing quantities into beer and wort and recording in days the first noticeable developments of organisms. Klöcker's detailed description for the manipulation of Pasteur flasks has also been reproduced.

The general style and clearness of presentation are superior to those of previous editions, and the book no longer suffers from clumsy phraseology. The illustrations are somewhat better in this edition, and seven photomicrographs of yeasts replace the drawings of former volumes. These photomicrographs, however, are of poor quality, owing to the use of too low a numerical aperture of the microscope objective, and fail to represent the cells as viewed under normal illumination. The magnification is not stated; presumably it is comparable in each reproduction. The index appears to have been compiled with care and will prove adequate.

In the reviewer's opinion this book fulfils its intended purpose and is worth the price charged for it. Perhaps the author rather over-estimates the value of pure cultures—it is still a debated point—and in this country it is the exception, rather than the rule, for brewers to make use of pure-culture yeast. English

brewers have possibly not persevered sufficiently with the selection and application of pure yeasts. One cannot altogether blame them, however, for not forsaking the tried and trusty friend for one so admittedly fickle as the pure culture.

F. M. CORY

MIKROSCOPISCHE METHODEN IN DER MIKROCHEMIE. By LUDWIG and ADEHEID KOFLER and ADOLF MAYRHOFER. With 21 figures and 12 pages of reproductions of photographs. Pp. vi + 134. Vienna and Leipzig: Haim & Co. 1936. Price 9RM., bound 10.80RM.

The book is divided into four sections: Micro-melting-point determinations, micro-sublimation, cryoscopic methods, and a short chapter on immersion liquids for the determination of refractive indices.

The micro-melting-point apparatus of Kofler and Hilbck (Abst., ANALYST, 1932, **57**, 130) is recommended, as it is more accurate than Klein's somewhat simpler heating-block (made by Reichert), for which a temperature correction is necessary. The Kofler and Hilbck apparatus is electrically heated and made to stand on the microscope stage, and the melting-point of crystals is observed under a magnification of 60 to 100 diameters, although, if necessary, magnifications up to 330 may be used. The temperature is read by means of either a thermo-electric couple or a thermometer calibrated on the apparatus on substances of known and sharply-defined melting-points. The apparatus is designed for incident light, and the advantages of the use of transmitted light are not mentioned. When transmitted polarised light is used, the melting-point of doubly-refracting substances is extremely easy to determine, as the illuminated crystals are simply blacked out.

A number of methods of micro-sublimation are described, and the importance of this most useful method in the identification of a very large number of compounds is emphasised by means of examples and references.

The book is clearly and simply written and well printed, and although most of the matter is not new, it is arranged in a convenient form for reference.

JANET MATTHEWS

CHEMICAL SYNONYMS AND TRADE NAMES. By WILLIAM GARDNER. Fourth Edition. Pp. 495. London: The Technical Press, Ltd. 1936. Price 31s. 6d.

The third edition of this valuable reference book was published in 1926, and reviewed in THE ANALYST (1926, **51**, 654); it then contained 355 pages with some 20,000 definitions and cross-references. Since then there has been a constant addition of new products to chemical industry, many of them having specially coined names, and this growth is reflected in the size of the present edition, which has been increased by 140 pages containing approximately 25,000 additional definitions.

The convenient alphabetical arrangement (without subordinate classification) of the previous editions has been retained, but the additional matter forms a second part, so that, for many products, a second reference to the book will be necessary. Although this is an easy matter, for the side-headings are printed in

bold type, yet, to prevent oversights, it would have been preferable to have had the new matter inserted in its alphabetical position in the old items. Probably the question of cost was the decisive factor that led to this arrangement, and as the work is issued at a reasonable price, this advantage outweighs that of complete re-arrangement of the whole of the material.

As in the former editions, the articles defined comprise not only commercial chemicals and raw materials for a wide range of industries, but also the trade names of a large number of proprietary articles.

Mr. Gardner is to be congratulated on having made readily accessible so much information that would be difficult to find elsewhere. Of course, everyone who looks for them may note omissions of substances with which he has specialised acquaintance, but, regarded as a whole, the work is remarkably complete and well fitted to serve its double purpose of a chemical dictionary and a commercial handbook. EDITOR

Publications Received

TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS. I. M. KOLTHOFF and E. B. SANDELL. Pp. xv + 749. London: Macmillan & Co., Ltd. Price 20s. net.

A TEXTBOOK OF ORGANIC CHEMISTRY. JULIUS SCHMIDT. Third Edition. English Edition by H. GORDON RULE. Pp. xxiv + 865. London: Gurney & Jackson. Price 25s. net.

LABORATORY EXPERIMENTS IN PHYSIOLOGICAL CHEMISTRY. A. K. ANDERSON. Pp. vii + 224. New York: Wiley & Sons, Inc.; London: Chapman & Hall. Price 7s. 6d. net.

CHEMISTRY OF THE COLLOIDAL STATE. J. C. WARE. Pp. xvi + 334. New York: Wiley & Sons, Inc.; London: Chapman & Hall. Price 18s. 6d. net.

WATER PURIFICATION CONTROL. E. S. HOPKINS. Pp. ix + 176. London: Baillière, Tindall & Cox. Price 8s.

SURVEY OF IMPORTS, RAW MATERIALS AND SYNTHETIC PRODUCTS. WITH SPECIAL REFERENCE TO THE HUMBER AREA. A. R. TANKARD. The City Laboratories, Hull. Pp. 54. Price 2s. 6d.