THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 2nd, Mr. John Evans, President, being in the chair.

Certificates were read in favour of:—William Reginald Bage, Albert R. Bonham, B.A.Sc. (Toronto), F.C.I.C., Henri Charles Philip Chapleau, B.A.Sc. (Montreal), Leo Cooksey, B.Sc. (Lond.), F.I.C., Douglas Eric Davis, B.Sc. (Lond.), F.I.C., Frederick Ellington, B.Sc. (Lond.), A.R.C.S., A.I.C., Edward Oscar Heinrich, B.S. (California), James Arthur Durham Hickson, B.Sc., A.I.C., Donald Robert Jackson, Daniel Carswell Macpherson, B.Sc. (Edin.), Florence Ellen Murphy, B.Sc. (Lond.), Temple Clifford John Ovenston, B.Sc., Ph.D. (Lond.), A.I.C., George Herbert Stott, M.Sc. (Liverpool), F.I.C., Basil C. L. Summers, B.Sc. (Lond.), Stanley Gordon Willimott, B.Sc. (Liv.), Ph.D. (Liv. and Cantab.), A.I.C.

The following were elected members of the Society:—Francis Highland Milner, B.Sc., A.I.C., Lewis Charles Nickolls, M.Sc. (Lond.), A.R.C.S., D.I.C., A.I.C., Corbet Page Stewart, M.Sc. (Dunelm), Ph.D. (Edin.), and Sidney Lionel Tompsett, D.Sc. (Lond.), Ph.D. (Glas.), A.I.C.

The following papers were read and discussed:—"The Chemical Examination of Furs in Relation to Dermatitis. Part VI—The Identification of Vegetable and other Dyes," by H. E. Cox, D.Sc., Ph.D., F.I.C.; "Testing for 'Sea Water Damage'," by W. M. Seaber, B.Sc., F.I.C.; and "A Contribution to the Iodimetric Titration of Tin," by F. L.Okell, F.I.C., and John Lumsden, B.Sc., A.I.C.

NORTH OF ENGLAND SECTION

A MEETING of the Section was held in Manchester on October 12th. The Chairman (Professor W. H. Roberts) presided over an attendance of forty-one.

The following papers were read and discussed:—"Colorimetric Determination by Photo-electric Cell," by N. Strafford, M.Sc., F.I.C.; "The Oxalates of Calcium, Barium, Strontium, and Magnesium," by J. Haslam, M.Sc., A.I.C.; and "Medicines Ancient and Modern," by U. A. Coates, M.P.S.

It was decided to send a letter of congratulation to Dr. J. T. Dunn on his recovery from illness.

ANALYTICAL METHODS COMMITTEE

Sub-Committee on Methods of Soap Analysis

The Sub-Committee which dealt with methods for the determination of Unsaponifiable Matter in Fats and Unsaponified Fat in Soaps, has now been reappointed as a Sub-Committee on Methods of Soap Analysis. The members of this Sub-Committee are Dr. H. E. Cox, F.I.C. (*Chairman*), and Messrs. E. R. Bolton, F.I.C., D. E. Davis, B.Sc., F.I.C., F. R. Ennos, B.Sc., F.I.C., N. Evers, B.Sc., F.I.C. (*Hon. Sec.*), B. D. W. Luff, F.I.C., and W. H. Simmons, B.Sc., F.I.C.

Sub-Committee on the Determination of the Freezing-point of Milk

A Sub-Committee has been appointed to take over the work of the British Standards Institution on this subject. The Sub-Committee consists of:—Mr. A. More, F.I.C. (*Chairman*), and Messrs. E. B. Anderson, M.Sc., F.I.C., G. D. Elsdon, B.Sc., F.I.C., J. Golding, D.S.O., F.I.C., J. A. Hall, B.Sc., A.R.C.S., Prof. J. C. Philip, M.A., D.Sc., F.R.S., and J. F. Tocher, D.Sc., F.I.C.

Obituary

HUGH CHARLES HERBERT CANDY

THE second son of the Rev. Herbert Candy, at one time Vicar of Orton, Leicester, Hugh Candy was educated privately and at University College, London, from which institution he graduated B.A. in 1883 and B.Sc. in 1888. His first appointment was as a master at Epsom College, and in 1895 he was appointed Lecturer in Physics and Chemistry at the London Hospital Medical School. He was also appointed Arnott Professor of Natural Philosophy at Queen's College, London. In 1911 he relinquished the teaching of physics at the London Hospital, in accordance with the newly-established regulations of the University, whereby a teacher of the University could only be "recognised" in one subject. Henceforth, therefore, his services were entirely devoted to the teaching and advancement of chemistry.

He was elected a member of the Society of Public Analysts in 1897, and served on the Council in 1909–1910. In 1898 he was elected a Fellow of the Institute of Chemistry and served as a member of the Council from 1916 to 1919.

While from his university education Candy might have been expected to have had equal loyalties to the arts and to science, I have the impression that, although he earned his living by teaching science, and, although he was the author of several standard scientific text-books, one of which—*Manual of Chemistry for Medical Students*, by Luff and Candy—has passed through seven editions, his real interests lay rather with the humanities. My reasons for this opinion are partly his great love of books—he was an indefatigable and discerning book-collector, being the possessor of many first editions of the English classics—and partly because he always, I thought, became more animated when a literary allusion was made than when a scientific problem was discussed. His literary interests and ability were well exhibited in his book published in 1924 on *Some New Discovered Stanzas*,

written by John Milton on Engraved Scenes Illustrating Ovid's Metamorphoses. Although the attribution of these stanzas to Milton has not received by any means universal acceptance, the arguments advanced by Candy in support of his contention made on many, including so critical a judge as the late Edmund Gosse, as favourable an impression as in the circumstances could be expected.

Not only was Candy a scholar of the old school, belonging to a time when university examinations, and particularly those of the University of London, were more broadly based than they are to-day; he was also indisputably a gentleman of the old school, passing through life with dignity and serenity, and with a never-failing courtesy to all and sundry.

Troubles, and of these he had more than his share—losing a son, the father of a young family, when on the threshold of his professional career, and later a much-loved and gifted daughter—though chastening, entirely failed to embitter him. His philosophy enabled him to ride all the storms of life—the boat swung but the anchor held—and it is pleasing to think of him in the evening of his day living peacefully and quietly in the company of his devoted wife, finding pleasure, as with all his modesty I feel he must have done, in the remembrance of good work well done, and comfort in those literary studies which his early training and cultured taste had taught him to appreciate and enjoy. Life and death being what they are, surely here is no occasion for tears or for beating the breast; rather an occasion for gratitude for so long and useful a life and for so noble an example.

In Cœlo Quies.

WILLIAM WRIGHT

PERCY ARTHUR WILLIAM SELF

PERCY ARTHUR WILLIAM SELF had been a member of our Society only since 1929, but by his death on May 24th, at the early age of 53, we have lost a chemist of unusual ability and mentality.

Self was a native of Williton in Somerset, and after serving a pharmaceutical apprenticeship in Yeovil, he entered the School of the Pharmaceutical Society in 1904, and completed his "Major" in 1906. He took his London B.Sc. degree in the same year, and became a Fellow of the Institute of Chemistry in 1912.

Shortly after completing his training he commenced work with the late E. F. Harrison, and in the course of a few years joined him as a partner. His work was always of a pharmaceutical character, and his published results indicate what a wide field of research that could cover.

He was a member of the Pharmaceutical Chemistry Sub-Committee of the British Pharmacopoeia Commission, and Chairman of the Pharmaceutical Chemistry Sub-Committee which dealt with the revision of the "Codex." As an examiner to the Pharmaceutical Society and, in pharmacognosy, to London University, his particular knowledge was of great assistance in educational matters, and gained him a wide circle of acquaintances.

His quiet retiring personality will live in the memory of many of his colleagues, but his unobtrusive helpfulness to men who had to leave their duties during the war will be known only to those who benefited by his many kindnesses.

C. E. SAGE

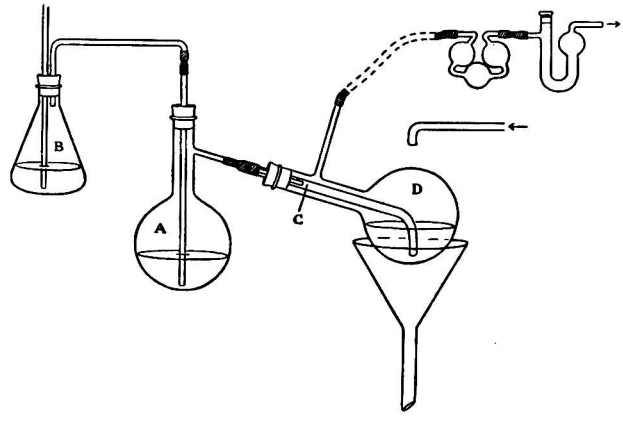
The Determination of Mercury in Viscera

By CLIVE NEWCOMB, D.M., F.I.C., S. RAJAGOPAL NAIDU, M.B., M.Sc., F.I.C., AND K. S. VARADACHAR, M.A., M.Sc.

THE method previously in use in this laboratory for the determination of mercury in viscera consisted in destruction of organic matter with potassium chlorate and hydrochloric acid and precipitation and weighing of the mercury as sulphide. There are many difficulties inherent in the method, especially when other metals, such as arsenic, iron, bismuth, copper or lead, are also present.

If arsenic is present, the separation of the mixture of the sulphides by means of dilute alkali is liable to peptise part of the mercuric sulphide, so that some of it passes through the filter. If bismuth, copper or lead is present and the mixed sulphides are treated with nitric acid, it is difficult to adjust the strength of the acid so as to dissolve the whole of the bismuth, copper or lead sulphide and none of the mercuric sulphide. The method can be made to work, but requires experience. If iron is present in considerable quantities, some iron sulphide is very likely to be co-precipitated with the mercury, and the last traces of it are difficult to remove.

The method described below relies on the volatility of mercuric chloride. The organic matter is destroyed by means of nitric and sulphuric acids, and the mercury is distilled off from the hot sulphuric acid in a stream of hydrochloric acid gas. At the temperature of boiling, or nearly boiling, sulphuric acid mercuric chloride can be completely distilled off.



A 500-ml. distilling flask, A, is fitted with a cork carrying a straight tube reaching to the bottom of the flask and connected with a wash bottle, B, containing concentrated hydrochloric acid. The side tube of the distilling flask is slipped into a wider tube, C, into which it enters to a distance of about three inches, and is held in position by means of a small piece of rubber tubing slipped over the two tubes. The tube, C, passes through a cork fitted to another 500-ml. distilling flask, D, containing about 300 ml. of distilled water, and is bent down at the end,

so that it nearly reaches the bottom. The side-tube of the flask, D, is connected with a potash bulb containing water and then with a Peligot tube also containing water. The other end of the Peligot tube is connected with a suction pump. The flask, D, is kept cool by means of a stream of water.

A suitable quantity of the visceral matter is placed in the 500-ml. distilling flask, A, disconnected from the rest of the apparatus, and concentrated nitric acid is added slowly without heating until a vigorous reaction sets in. As the reaction subsides further quantities of nitric acid are added till digestion is complete, and the whole has become a uniform yellow solution. The flask is then fitted with the cork and tube leading to the bottom of the flask and connected with the absorption part of the apparatus, as shown in the diagram. Suction is begun by the filter pump and about 50 ml. of strong sulphuric acid are added slowly through the long tube. The flask is then heated until white fumes begin to appear inside the flask. Any tendency to char is prevented by adding a few drops of strong nitric acid from time to time. (The current of air passing through the sulphuric acid prevents the fumes from attacking the corks and at the same time hastens the destruction of the organic matter.)

The heating is then stopped, and the contents of the absorption flask, the potash bulb and the Peligot tube are filtered into a beaker. This filtration is necessary to free the solution from small quantities of fatty acids that distil over. The filter is washed, and the washings are added to the filtrate. This liquid, which contains nitric and nitrous acids, is treated with potassium permanganate till pink, to oxidise the nitrous acid, and then decolourised with oxalic acid. Hydrogen sulphide, washed by passing through water, is passed into the liquid and the mercury is precipitated as sulphide. The precipitate, which accounts for about a third of the total mercury, contains a fair amount of sulphur. The precipitate is allowed to settle and the supernatant liquid decanted on to a filter. The precipitate is washed several times with water and the washings decanted on to the filter, the main bulk of the precipitate being retained in the beaker. This is dissolved in bromine water and the solution is poured on to the filter, the filtrate and washings of the beaker and filter being collected in a flask. This bromine solution is kept until a later stage.

A fresh quantity of distilled water is placed in the absorption flask and tubes and the apparatus is re-connected. This time the wash-bottle containing hydrochloric acid is connected with the tube in the distillation flask. Suction and heating are started and continued for three hours. At the end of the period the apparatus is disconnected, and the contents of the absorption flask and tubes are washed into a beaker. The mercury in this solution is precipitated as sulphide, filtered off, washed and dissolved in bromine water, as before. The two bromine solutions are now mixed and boiled till free from bromine. The solution is acidified with hydrochloric acid and the mercury is re-precipitated as sulphide, which is filtered through a Gooch crucible, washed, dried and weighed.

The procedure of dissolving the precipitate of mercuric sulphide in bromine water, filtering, boiling off the bromine and re-precipitating as sulphide is very effective in getting rid of the sulphur, and is preferable to washing the precipitate with carbon disulphide.

The method was first tried with pure mercuric chloride solution, and the following results were obtained:

Mercuric chloride taken, mg. ..	131·0	176·0	169·0	70·0
,, ,, recovered, mg. ..	130·0	176·0	167·5	68·6

In these experiments the preliminary destruction of organic matter with nitric acid was omitted.

The method was then tried on viscera to which known quantities of mercuric chloride had been added, with the following results:

Mercuric chloride added, mg. ..	14·5	14·5	20·4	30·0	120·4	120·4	120·4	130·9	130·9	196·4
Mercuric chloride recovered, mg.	14·5	13·8	20·2	30·5	118·8	119·6	119·6	129·2	129·5	194·0

Thus, with quantities up to about 200 mg. of mercuric chloride the method is fairly accurate. With larger quantities the distillation was not completed in three hours. For example, with 550 mg. of mercuric chloride added, only 430 mg. were recovered.

The method was then tried on viscera containing mercury, bismuth, copper, iron and lead, respectively, in addition to mercury, and the following results were obtained:

Mercuric chloride taken mg.	Added metal in solution	Mercuric chloride recovered mg.
150·0	Bismuth	148·5
167·5	Copper	165·0
167·5	Iron	165·0
133·6	Lead	131·6

The method was also tried on mixtures of arsenic and mercury. From inorganic solutions arsenic, if present in the tervalent condition, distils over with the mercury. But, if the arsenic is oxidised to the quinquevalent condition by means of nitric acid before distillation, mercury alone distils over and arsenic is left behind in the sulphuric acid, in which it can be quantitatively determined. Thus an inorganic solution containing both mercury and arsenic, after oxidation with nitric acid and distillation, yielded the following results:

Added { 31·8 mg. As_2O_3 / 150·0 mg. $HgCl_2$ } Recovered { 30·2 mg. As_2O_3 / 147·4 mg. $HgCl_2$ }

With viscera containing both mercury and arsenic, the method of destruction of organic matter employed above converts the arsenic to the quinquevalent condition. Mercury alone distils over and arsenic is left behind in the distillation flask. The results of a determination are given below:

Added { 31·8 mg. As_2O_3 / 150·0 mg. $HgCl_2$ } Recovered { 30·5 mg. As_2O_3 / 147·5 mg. $HgCl_2$ }

The method described above is thus seen to be of advantage in the determination of mercury in viscera, especially in the presence of other heavy metals.

The possibility of a loss of mercury when excess of bromine is boiled off from a dilute mercury bromide solution had previously been investigated by us (cf. *Annual Report of the Chemical Examiner to the Government of Madras*, 1934; ANALYST, 1935, 759), and was further investigated in connection with this paper.

The recovery of nearly all the mercury in this method shows that the loss, if any, cannot be great. The following tests were made:

(i) By distilling the solution of mercuric bromide and bromine until all the colour of the bromine had disappeared and testing the distillate for mercury. It was found that with dilute solutions, up to 1 in 1000 (200 mg. of mercuric chloride in 200 ml. of water), no visible precipitate of mercury sulphide could be obtained from the distillate. With stronger solutions some loss occurred. This loss could be prevented by the addition of potassium chloride to the solution. In one experiment 600 mg. of mercuric chloride were precipitated as mercuric sulphide and dissolved in 200 ml. of water by excess of bromine, 5 g. of potassium chloride were added, and the mixture was distilled. The excess of bromine had boiled off when 10 to 15 ml. had distilled over, but the distillation was continued until 100 ml. of distillate had been collected, and in this no mercury could be detected.

(ii) By testing the final precipitate of mercuric sulphide for sulphur by extraction with carbon disulphide. No loss of weight of the precipitate was caused by this extraction and the carbon disulphide left no residue on evaporation.

To make sure that all the arsenic was retained under the conditions of the method a solution of arsenious oxide in sulphuric acid was oxidised and distilled, as for mercury, by this method. No precipitate was obtained on passing hydrogen sulphide through the distillate, and the Reinsch test was negative.

CHEMICAL EXAMINER'S LABORATORY
MADRAS

The Determination of Small Amounts of Boron by means of Quinalizarin

BY G. STANLEY SMITH, B.Sc., A.I.C.

THE intensely coloured solutions of many hydroxyanthraquinones in concentrated sulphuric acid show, on the addition of boric acid, a marked change of colour that can be used for their identification. The colour-change has also been used by Feigl[1] for the microchemical detection of boric acid, quinalizarin furnishing the most sensitive test.

Feigl's procedure is as follows:—Evaporate to dryness one drop of the weakly alkaline solution in a micro-crucible, add 2 to 3 drops of a 0·01 per cent. solution of quinalizarin in concentrated sulphuric acid and warm gently. In the presence of boric acid the violet solution becomes blue. The method is sensitive to 0·06γ of boron. It is spoilt by fluorides and also by nitrates, ferricyanides and other oxidising agents, but the latter may be prevented by previous ignition from interfering. Metallic salts lower the sensitivity only slightly.

A test that has to be conducted in a medium of concentrated sulphuric acid has not such general applicability as one that can be made in more dilute acid. During an investigation into the colour changes in various concentrations

of sulphuric acid it was found that the most sensitive change occurred in about 92 to 94 per cent. by weight of H_2SO_4, and that the colour of the solution might be made the basis of a quantitative determination of boric acid. The change in this and slightly lower concentrations is from reddish-violet or pink to blue and, consequently, is more easily detected than a change from bluish-violet to blue.

Boric acid produces a change of colour in all concentrations of sulphuric acid down to about 44 per cent. by weight. The sensitivity at first increases as the sulphuric acid concentration is lowered until about 93 per cent. is attained and then decreases. Under 85 per cent. the decrease is rapid and the sensitivity in the lower concentrations is very poor.

The minimum amount that can be detected appears to be about 0·012γ of boric acid or 0·002γ of boron, one drop each (0·02 ml.) of very dilute solutions of boric acid and quinalizarin in 93 per cent. sulphuric acid being used.

On the gradual addition of water to a solution of quinalizarin in concentrated sulphuric acid the bluish-violet colour changes progressively through various shades of reddish-violet and red to orange. The presence of boric acid counteracts to some extent the colour change produced by water; thus, a solution of quinalizarin in 87·5 per cent. sulphuric acid matches one in 69 per cent. sulphuric acid containing 0·01 g. of boric acid per 10 ml. In concentrations below 78 per cent. an excess of boric acid fails to give a blue colour.

TABLE I

COLOUR CHANGES IN VARIOUS CONCENTRATIONS OF SULPHURIC ACID

Volume of solution, 10 ml.; quinalizarin, 0·25 mg.

Sulphuric acid, per cent., by weight	Colour	Addition of 0·01 g. boric acid
99·5 to 97·5	Bluish-violet	Blue
94	Reddish-violet	Blue
88 to 80	Red	Blue
78	Red	Bluish-violet
73 to 69	Red	Red (slight violet tinge)
55	Orange	Pink
44	Pinkish-yellow	Orange

TABLE II

SENSITIVITY IN VARIOUS CONCENTRATIONS OF SULPHURIC ACID

Volume of solution, 10 ml.; quinalizarin, 0·05 mg.

Sulphuric acid, per cent., by weight	Minimum quantity in mg. of boric acid to give	
	definite change	blue colour
99·5	about 0·01	about 0·03
97·5	,, 0·005	,, 0·03
94 to 92	,, 0·001	,, 0·04
87·5	,, 0·005	,, 0·25
78	,, 0·2	,, 20

The rapidity of the colour-change increases as the sulphuric acid concentration decreases, unless a large excess of boric acid is added. In concentrated sulphuric

acid a permanent colour, bluish-violet or blue, is obtained only after several hours; in 92 to 94 per cent. five minutes is sufficient; and in 87·5 per cent. the change is practically immediate.

The colours, when fully developed, are stable almost indefinitely, if the solutions are kept in closed tubes to avoid absorption of water.

The effect of heat is to develop a pink shade, which tends to mask the effect due to boric acid.

The colour appears to be specific for boric acid in the absence of such substances as nitrates and dichromates, fluorides, and those that give very noticeable colours in sulphuric acid. None of the common metals spoils the test, so that it is quite suitable for the detection of boron in alloys and minerals. The sample may be attacked by sodium hydroxide, by fusion with alkali carbonate or disodium phosphate and metaphosphoric acid, followed by careful solution in sulphuric acid, or by direct solution in sulphuric acid under a reflux condenser. Also, the test may be applied to a distillate obtained by the usual method, since methyl alcohol may partly or wholly replace the water in the test solution.

The method employed in estimating boric acid consists in comparing the colour of a solution obtained from the material or solution under examination with the colours of other solutions containing known amounts of boric acid, the sulphuric acid and quinalizarin concentrations being the same in all. When large proportions of other elements are present, the solutions compared should contain approximately the same amounts of these elements. The chief advantage of using somewhat diluted sulphuric acid is that the necessity for making the solution under examination alkaline and evaporating it to dryness is avoided.

The method has been applied particularly to the determination of boron in aluminium-silicon alloys.

The behaviour of the solutions in 93 per cent. sulphuric acid towards petroleum spirit is interesting. On shaking the reddish-violet and blue solutions with A.R. petroleum spirit, 40/60°, the colours appear to be practically unchanged, but if petroleum spirit, 100/120° is used, the reddish-violet boric acid-free solution turns a blood-red colour and the blue solution containing boric acid turns yellowish-green. The petroleum spirit layers remain colourless. This effect has been obtained with petroleum spirit from various sources.

METHOD.—Suitable concentrations of sulphuric acid for the colorimetric determination of boric acid are obtained by diluting 9 and 4 volumes, respectively, of the concentrated acid with 1 volume of water. The colour-change in the latter concentration permits of the determination of about 5 or 6 times the amount of boric acid that can be determined in the former concentration, but the sensitivity is lowered proportionally.

The sulphuric acid should be A.R. or Analar grade, 97·5 to 99·5 per cent. by weight. It should be free from nitrates, and 0·0005 per cent. solutions of quinalizarin in the diluted acids should have stable pink colours, though of different shades.

Determination of 0·001 *mg. to* 0·040 *mg. of boric acid.*—Standard solutions:—Boric acid, 0·0050 g. per l. of H_2SO_4(9 : 1); quinalizarin, 0·01 g. per 100 ml. of H_2SO_4(9 : 1).

Transfer, by means of a pipette, 1 ml. of the aqueous solution to be tested to a small comparison tube or test-tube, add 9 ml. of concentrated sulphuric acid from a burette, mix and cool the solution. In another tube place the same volume of 9 : 1 sulphuric acid and add to each 0·5 ml. of the quinalizarin solution. Mix the solution well and compare the colours. If a reddish-violet, bluish-violet or blue colour forms within five minutes and if interfering substances are absent, boric acid is present. A pure blue colour implies the presence of at least 0·04 mg. of boric acid in the quantity of material tested.

Assuming that a reddish-violet or bluish-violet colour is produced, it may be matched with standards. In several similar tubes place different volumes of the standard boric acid solution, at most 8 ml., and make up each to the same volume as the test solution with H_2SO_4 (9 : 1). Add to each 0·5 ml. of the quinalizarin solution, mix and leave for 5 minutes. One of these may be slightly bluer and one slightly pinker than the test solution. Further standards should now be prepared and an exact match obtained.

The method is accurate to a millionth of a gram of boric acid over the range 1 to 40γ, provided that the sulphuric acid concentrations in all the solutions are approximately the same. This condition is realisable in practice, since an error of as much as 5 per cent. in measuring the water for any one test causes the formation of a colour corresponding with that given by a decrease of the boric acid content to an extent just observable, that is to say, of about 1γ. When standardised apparatus, pipettes and burettes for small volumes, and measuring cylinders for the stock solutions are used and all the solutions are made up from the same batch of sulphuric acid, the concentrations of the solutions used for matching are sufficiently close.

If less than 1γ boric acid is indicated, the original solution may be concentrated somewhat, after being made alkaline, and the test applied to the stronger solution.

Quantities of 0·005 *mg. to* 0·25 *mg. of boric acid.*—Standard solutions:—Boric acid, 0·0250 g. per l. of H_2SO_4 (4 : 1); quinalizarin, 0·01 g. per 100 ml. of H_2SO_4 (4 : 1).

Mix 2 ml. of the aqueous solution to be tested with 8 ml. of concentrated sulphuric acid, add 0·5 ml. of the quinalizarin solution, and proceed as before, using 4 : 1 in place of 9 : 1 acid. The accuracy is about 5γ over the range 5 to 250γ.

Boron in Aluminium-silicon Alloys.—Boron is not a common constituent of aluminium-silicon alloys, but its occasional use as a modifying agent and the requirements of specifications, such as B.S.S., L. 33, necessitate an accurate method for the determination of small quantities of this element. Existing methods, with the possible exception of spectrographic methods, are tedious or untrustworthy. It is doubtful whether all the boron can be distilled as methyl borate in the presence of large quantities of aluminium salts and silica, and the removal of the aluminium before the distillation by means of ammonia is unsatisfactory, since it does not serve as a separation from borates; moreover, it is almost impossible to filter the solution, unless the silica has been removed by methods necessarily causing loss of boric acid by volatilisation and leaving some of the boron associated with the silica.

If the possible boron-content of the material is disregarded, an error may be caused in the silicon determination by reason of the volatility of boron fluoride.

By proceeding as in Callendar's method for silicon[2] a clear solution may be

obtained, suitable for the determination of boron by means of quinalizarin. Dissolve the sample and a boron-free alloy in separate crucibles as follows:

Treat 0·5 g. of the fine drillings with 20 ml. of 10 per cent. sodium hydroxide solution in a large nickel crucible fitted with a lid. After the initial attack is over wash down the lid and sides, evaporate the solution nearly to dryness on the hot-plate, add about 20 ml. of water, boil for a short time, and pour the solution into 30 ml. of 60 per cent. sulphuric acid. Wash out the crucible with a little acid and then several times with water, removing any solid particles. Make up the solution to 100 ml. with water.

Place 1 ml. of each of the solutions so obtained in small comparison tubes, add 8 ml. of concentrated sulphuric acid, mix and cool the solutions, and add 0·5 ml. of 0·01 per cent. quinalizarin solution. Compare the colours after 5 minutes and determine any boron present by the method given above, except that 1 ml. of the solution of the boron-free alloy should be added to each standard that is made up.

The method is suitable for quantities of boron down to 0·01 per cent. of the alloy.

REFERENCES

1. F. Feigl and P. Krumholz, *Mikrochem., Pregl Festschrift*, 1929, p. 77; F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, 2nd Edition, 1935, p. 331.
2. L. H. Callendar, ANALYST, 1932, **57**, 500.

A.I.D. MATERIALS TEST HOUSE
R.A.F. No. 1 STORES DEPÔT
KIDBROOKE, S.E.3

The Application of Controlled Potential to Microchemical Electrolytic Analysis

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

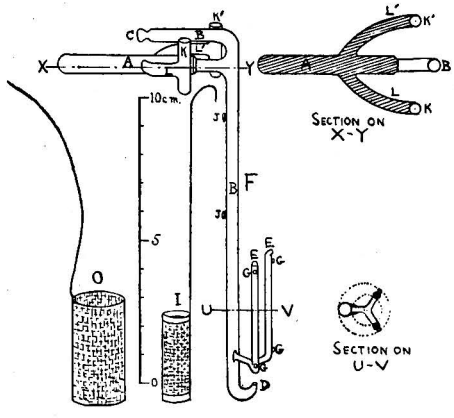
(*Read at the Meeting on November* 6, 1935)

THE electrolytic method has been applied by Pregl[1] with considerable success in gravimetric microchemical analysis. Pregl describes the determination of copper, and the method has since been tested[2,3,5,10] and extended to silver,[7] cadmium,[7] mercury,[7,8] lead,[12] nickel,[4,10] and cobalt.[4]

Microchemical electrolytic methods should lend themselves particularly well to separations in which the potential difference between the anode and cathode is controlled without the use of an auxiliary electrode. Hitherto, however, no work appears to have been done in this direction. The relatively small currents employed even in determinations requiring no more than ten to fifteen minutes make it possible to keep the potential difference due to ohmic resistance in the electrolyte small, provided that a relatively large anode surrounding the cathode is employed. By this means, too, and by the use of suitable depolarisers, it should be possible to maintain the variation of the anode potential within narrow limits.

The electrodes described by Pregl, which consist of a cylindrical gauze cathode with a central wire anode are excellent for the condition prescribed by him of a boiling electrolyte, the stream of steam bubbles rising from the anode causing vigorous circulation and freeing the electrolyte from dissolved oxygen. For the purpose under review they are, however, unsuitable. The use of depolarisers, which we recommend, makes boiling temperature unnecessary, and, to compensate for the absence of this, stirring is effected by means of bubbles of an indifferent gas.

FIGURE 1



The assembly of the frame and the electrodes we have designed is explained by Figs. 1 and 2. Vertical and square-on horizontal dimensions are shown to scale. The inner or working electrode I (Fig. 1) is the ordinary Pregl cathode with the beads removed. The outer electrode, the body of which is made entirely of thin gauze, is explained fully by O (Fig. 1). F is the frame on which the electrodes are placed. It will be seen that it is built upon the inlet tube, B, of the gas used for stirring. The entrance, C, is opened to a nipple, the outlet, D, being turned up into a capillary jet. Near the top of B is sealed a glass rod, A, which is held by the boss-head, G, on the small stand shown in Fig. 2. The rod, A, carries two arms, L and L', to which mercury cups, K and K', are attached. The arrangement of A, L, L', K and K' is shown to scale in plan on a level with the position in the view. Near the bottom of B the 2-mm. rods, E, are fitted to form a cage into which the working electrode, I, can be dropped, so as to sit securely, electrical connection being made by means of the mercury cup, K'. The outer electrode is held permanently in position by the beads, G, sealed on to the rods E, as shown in the figure, the connecting wire being twisted round the beads, J, and dipped into the mercury cup, K. The cups, K and K', are permanently connected by platinum-tipped wires to the terminals T and T' fitted to the stand (Fig. 2). Horizontal dimensions may be taken from the sectional plan U–V. The electrolysis vessel is a test-tube ("Monax") of internal diameter 2 cm., cut to a length of about 10 cm., and holding about 12 ml. to the top of the electrodes. It rests on the bottom of a 100-ml. beaker, which serves as a water-bath, and it is held securely in position by the frame, F. The ring, R, which supports a gauze, and to which the micro-burner, M, is also attached, is so constructed that it may be swung aside.

METHOD OF WORKING.—The electrodes having been put in position, the solution is placed in the test-tube, which is raised from below until the frame touches the bottom. The water-bath is likewise raised from below, and the ring, R, swung into position. Water is then added until the electrodes are covered, and the gas used for stirring is admitted, its flow being adjusted by means of a screw clip near the apparatus. The gas is taken from a hydrogen, nitrogen, or

carbon dioxide cylinder, as the case may be, and in order that no inconvenient pressure may arise, it passes through a T-tube, the open end of which dips into a boiling-tube containing a suitable amount of water. The water-bath is raised to the required temperature, the current is switched on, and the voltage between the electrodes is raised from zero to the correct value by moving the slider, S (Fig. 5). This value is maintained until the metal is exhausted, the current usually falling to about one-tenth of its original value. The test-tube is then

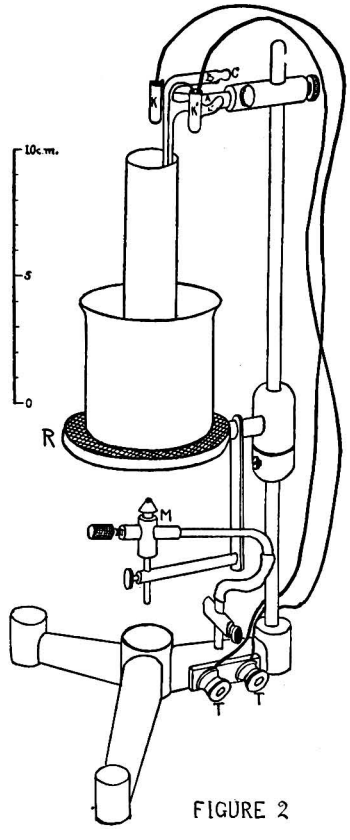


FIGURE 2

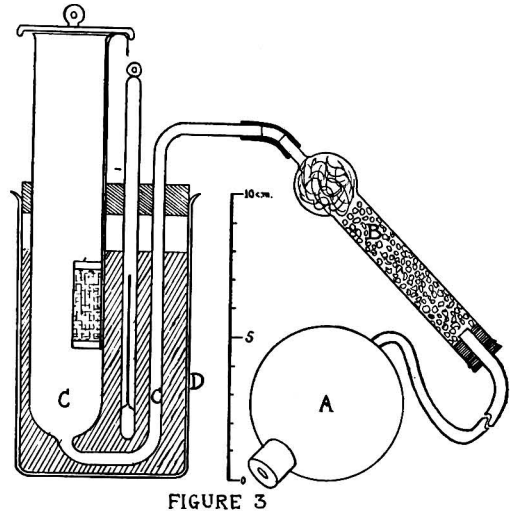


FIGURE 3

washed down with a fine jet of water, and the residual current is maintained for a few minutes. The water-bath is now removed and replaced by a beaker of cold water, current and stirring gas being left on. When the electrolyte is at room temperature, first the water-bath and then the test-tube is lowered, while the exposed parts of the inner electrode are sprayed by a jet of water until the whole has been washed. The inner electrode is then removed by a platinum hook, dipped rapidly in turn into water, alcohol and ether, and dried by holding it in the hot air above a bunsen flame for a few minutes, or preferably in the dryer (Fig. 3). The end which has dipped into the mercury contact cup is then heated to redness to remove traces of mercury which may adhere to the wire (see also Okáč[4]). The electrode is allowed to cool for about a minute in the air, and is then transferred to the micro-balance, and, after the lapse of fifteen minutes,

weighed. During this time the side doors of the balance case are kept open, whilst the large outer case in which the balance is mounted is closed. A counterpoise for the electrode is used. A convenient tool, shown in Fig. 4, for carrying the electrode and placing it across the hooks of the (Bunge) microchemical balance without handling was devised. The technique of transferring the electrode from the platinum hook to the silver-plated tool is readily acquired.

The drying apparatus, to which reference was made above, is shown to scale in Fig. 3. In this a stream of air from the hand-bellows, A, is blown through the tube, B, which is filled with calcium chloride and cotton wool, and then through the glass U-tube, C, which is heated to over 100° C. in a bath, D, of boiling water and glycerin. The electrode is hung in the wide limb, as shown, while the stream of warm dry air is passed over it. One minute is sufficient to dry most deposits to constant weight. When not in use the tube is conveniently kept covered by means of a crucible lid.

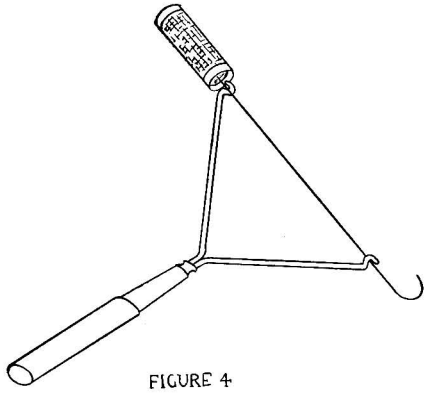


FIGURE 4

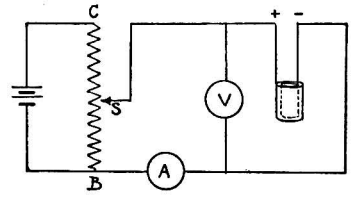


FIGURE 5

The electrical circuit employed is shown in Fig. 5. It will be seen that current from two accumulators is passed through the rheostat, BC, the voltage required being tapped off between B and the slider, S. The voltmeter, V, was a high-resistance instrument (50,000 ohms). If a low resistance instrument is employed, allowance may possibly have to be made for the current flowing through it.

Since depolarisers are employed during the application of the method described, we have thought it useful to make a study of the anodic depolarisation produced by the sulphates and hydrochlorides of hydrazine and hydroxylamine under varying conditions of current and temperature. We have also examined the effect of the addition of salts of copper and silver to the acid electrolyte. We have found that hydrazine salts appear to be efficient under all conditions; the depolarising efficiency of hydroxylamine is appreciably smaller, but is improved by the presence of chloride and of copper ions. Figs. 6*a* and 6*b* show the results we have obtained. Currents of varying strength were passed between the electrodes described by us,[13] the electrolyte consisting of 80 ml. of a 2·5 per cent. solution of copper sulphate crystals to which 5 ml. of 2 *N* sulphuric acid and 5 ml. of depolariser solution were added. According to the experiment the

depolariser contained 2 per cent. of either the sulphate or the hydrochloride of hydrazine or hydroxylamine. The outer electrode was made the anode and the potential difference between it and a saturated calomel electrode with sodium sulphate as connecting liquid was measured as described by us.[14] Logarithms of the current density are plotted as abscissae, and the potential differences between the anode and the auxiliary electrode as ordinates. The actual values of the current density have also been entered. The latter have been arrived at by dividing currents by the overall single surface area of the electrode employed. It will be seen from Fig. 6*a*, by comparing the no-depolariser line with that obtained with hydrazine sulphate, that the latter reduces the polarisation at ordinary temperature by about 1·3 volt. The depolarising efficiency of hydrazine hydrochloride is slightly smaller than that of the sulphate. The depolarising efficiency of hydroxylamine salts is smaller and, in the absence of copper ions, smaller still. In all cases, as shown by Fig. 6*b*, rise of temperature increases depolarising efficiency, this being particularly marked for hydroxylamine salts at low current density.

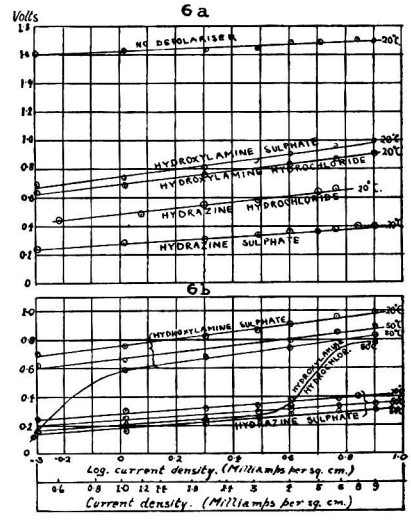


FIGURE 6

The micro-method described may be employed for copper depositions and other determinations to which the Pregl method is applicable, even when boiling temperature is not maintained. In addition, it has been applied successfully to the separation of bismuth from lead and that of copper from tin and other metals in chloride solutions, which processes cannot be carried out with Pregl's electrodes and without the control of cathode potential. These methods will be described later.

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The Micro-Electrolytic Determination of Bismuth and Lead and their Separation by Graded Potential

By A. J. LINDSEY, M.Sc., A.I.C.

(*Read at the Meeting, November* 6, 1935)

No methods for the quantitative micro-electrolytic deposition of bismuth or for its separation from lead have yet been described. The present investigation has resulted in a satisfactory technique for the separation and determination of both metals. Brantner and Hecht[1] did not recommend the micro-electrolytic deposition of lead as dioxide, but it should be noted that they used a platinum micro-crucible as the anode and were not able to control the conditions sufficiently well to ensure reproducible results. The electrolysis apparatus of Pregl may be used for the determination of lead as dioxide at the boiling-point of the solution, and the results are in agreement with those obtained by the technique later to be described. The determination of bismuth alone and its separation from lead cannot be effected with Pregl's electrodes.

The anodic deposition of lead from a nitric acid solution as dioxide in the presence of bismuth always results in the occlusion of bismuth in the deposit. Previous work upon the separation has been carried out on a macro-scale by Sand,[2] Lassieur[3] and Collin.[4] In each case a reducing agent was added to the solution to prevent the anodic deposition of lead, and the cathodic deposition of bismuth was controlled by the method of graded potential. As reducing agent Sand used glucose or tartaric acid, Lassieur hydroxylamine, and Collin hydrazine; but whereas the two former authors subsequently deposited the lead as metal, the last destroyed the hydrazine and deposited the lead as dioxide. This method has been modified to suit the micro-apparatus described in the previous paper, and the general method outlined therein has been followed.

The Determination of Bismuth.—To the bismuth solution, containing up to 6 mg. of bismuth, 1 ml. of nitric acid (sp.gr. 1·42), two drops of hydrazine hydrate solution (50 per cent.), and sufficient water to make a volume of 12 ml. are added. The solution is heated to 60 to 70° C. in the water-bath of the apparatus previously described (p. 740), and electrolysed at an anode-to-cathode potential of 0·8 volt. The current falls during the electrolysis from about 80 milliamperes to about 10 milliamperes. Nitrogen stirring is employed. After 10 minutes the tube is washed down with a fine jet of water, and the potential across the cell is increased to 0·9 volt. After a further 3 minutes the tube is cooled by replacing the hot water-bath by a cold bath, and the electrolysis is terminated by rapidly replacing the tube by a shorter tube containing distilled water. The electrode is dipped successively into alcohol and ether and transferred to the dryer for one minute. The deposit and cathode are weighed as described previously. The following analytical results were obtained using the above method.

Bismuth taken, 5·595 mg.
Bismuth found, 5·62, 5·60, 5·60 and 5·62 mg.

The deposit was in each case dark grey and firmly adherent to the cathode. The deposits were removed by solution in nitric acid.

THE DETERMINATION OF LEAD.—To the lead solution, containing up to 6 mg. of lead, are added 2 ml. of nitric acid (sp.gr. 1·42), and the whole is diluted to about 12 ml. in the apparatus previously described, the previously weighed inner electrode being made the anode. The solution is heated almost to boiling by means of the micro-burner, and is kept at this temperature during the whole time of electrolysis. Stirring is effected by means of a nitrogen stream. The anode-to-cathode potential necessary is 1·0 volt, and the current passing is from 120 to 200 milliamperes. The potential is not critical, and higher values may be used if necessary to maintain the current density. After 7 minutes the sides of the tube are washed down with a jet of water, and in another 3 minutes the electrolysis is terminated by rapidly replacing the tube by a shorter one containing distilled water. The electrode is then dipped in turn into alcohol and ether and transferred to the dryer for one minute. The deposit and cathode are re-weighed as before described. Determinations of lead made according to the above procedure are slightly high. This is in harmony with the findings of previous workers,[5,6,7,8,9] and from the results a factor appropriate to the method was calculated. No lead could be detected in the residual liquid after making it alkaline with ammonia and then adding hydrogen sulphide.

The following results were obtained by the above method:

Lead taken mg.	Lead dioxide found mg.	Lead found mg.
4·068	4·76	4·09
	4·71	4·05
	4·74	4·08
	4·73	4·07
	4·72	4·06
	4·73	4·07
	Mean 4·73	

From the mean of the six determinations of the dioxide the factor 0·860 was calculated, from which the values of column three were obtained.

THE SEPARATION OF BISMUTH AND LEAD.—To the solution containing not more than 6 mg. of each metal, are added 1 ml. of nitric acid (sp.gr. 1·42) and two drops of hydrazine hydrate solution (50 per cent.). The volume is made up to 12 or 13 ml., and the solution is electrolysed at 60 to 70° C., with nitrogen stirring. The anode-cathode potential is kept at 0·8 volt, and the current density falls during the electrolysis from an initial value of about 70 milliamperes to about 10 milliamperes. After 10 minutes from the start the tube is washed down, and the electrolysis is continued at an anode-cathode potential of 0·9 volt for another 2 minutes, when the hot water-bath is replaced by a cold one. With the current still on, the test-tube is rapidly replaced by a shorter one containing about 12 or 14 ml. of distilled water. The cathode is then removed, and after being dipped into alcohol and ether is dried as usual.

The deposit and cathode are weighed as previously described.

The solution from which the bismuth has been removed is transferred to a 50-ml. tall-form beaker, some of the water which has been used for washing the electrodes being used to effect complete transference. Fifty per cent. sodium hydroxide solution is added, drop by drop, until the precipitate redissolves, after which a few (10 to 20) mg. of sodium peroxide are added, and the beaker is heated (with a cover) until no more oxygen evolution is apparent. The whole is neutralised with concentrated nitric acid, and an excess of 4 ml. of acid is added. Finally, the remainder of the washing-water is transferred. With care the volume may be kept as low as 30 or 35 ml. The solution is electrolysed in the beaker at a temperature just below boiling-point, with nitrogen-stirring and an anode-cathode potential of 1·2 volt. This value is not critical, and a higher potential may be used. The current may be as great as 300 milliamperes. No water-bath is used, the beaker being heated directly by means of the micro-burner. After 12 minutes the beaker is washed down, and in a further 3 minutes deposition is complete. If, however, the electrode is weighed, the result is always found to be very high, owing, no doubt, to sodium salts occluded by the dioxide. Accordingly an electrolysis test-tube containing 2 ml. of nitric acid and 12 ml. of water is placed in the position occupied by the beaker, and the current is reversed to redissolve the dioxide. When the centre electrode is free from deposit the current is reversed again, and the lead deposited as described earlier. The following results were obtained by this method:

Metal taken		Found		
Bismuth mg.	Lead mg.	Bismuth mg.	Lead dioxide mg.	Lead mg.
1·11	4·11	1·09	4·77	4·10
2·22	4·11	2·26	4·78	4·11
3·36	4·11	3·36	4·83	4·15
5·65	4·11	5·62	4·77	4·10
5·65	4·11	5·62	4·75	4·09

The values recorded in the last column were calculated from the weights of lead dioxide found, by means of the factor (0·860) determined earlier.

I wish to express my thanks to Dr. H. J. S. Sand for his suggestions and continued interest in this work.

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Notes

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

A NOTE ON THE ANALYSIS OF IODINE OINTMENTS

WE have recently examined several samples of iodine ointment, the genuineness of which was in question, and the resulting cases were reported among the Legal Notes (ANALYST, **1935, 60**, 245). Since then we have received a number of queries as to the methods of analysis we adopted. It would, therefore, appear that a brief résumé of these methods might be of value, particularly in view of the fact that we ourselves met with some difficulty in finding satisfactory methods from the literature on the subject.

There are two main varieties of iodine ointment—the ordinary and the stainless. For the former the **1914** B.P. required iodine 4 per cent., potassium iodide 4 per cent., glycerin 12 per cent., and prepared lard 80 per cent.—a formula modified in the B.P.C. 1934 by replacing the base of glycerin and prepared lard by simple ointment, in order to avoid the combination of the iodine with the fatty base discussed later. For the stainless ointment the B.P.C. 1934 requires iodine 5 per cent., arachis oil 15 per cent. and yellow soft paraffin 80 per cent. In addition, there are several similar proprietary ointments, the main feature of which is that the iodine is in organic combination with a fatty base. The iodine-content of these is often declared on the label.

The methods described by Evers and Elsdon (ANALYST, 1922, **47**, 197) for determining the free iodine and potassium iodide in the B.P. ointment are not adequate, as they do not take into consideration the iodine in organic combination. Pullen (*Pharm. J.*, **1922, 35**, 610) has shown that in an ointment prepared according to the B.P. formula combination occurs between the free iodine and the lard, the uncombined iodine being reduced by a third in several months, although the total quantity remains practically unchanged. Fried (*Yearbook of Pharmacy*, 1915, 270) and Warren (*ibid.*, 1918, 334) have shown that equilibrium between the free and combined iodine in the ointment is attained after about 30 per cent. of the free iodine has been absorbed, and that the presence of potassium iodide is essential to limit this change. In justice to the manufacturer, it is necessary to ascertain the total iodine actually used in compounding, which will naturally include both the free halogen and that which has subsequently combined with the base.

The free iodine and the potassium iodide are readily determined by the methods of Evers and Elsdon (*loc. cit.*). For the determination of the total iodine the method of Thompson and Snyder (*Yearbook of Pharmacy*, 1917, 102), which consists in saponification of the ointment with alcoholic potash, removal of the unsaponifiable matter, and subsequent liberation of the iodine with hydrogen peroxide in acid solution, was found to be unsatisfactory; in fact, the authors themselves admit that alcoholic potash does not take up the iodine absorbed by the ointment base. Nor was alkaline fusion (Middleton, *Quart. J. Pharm.*, **1929, 12**, 536), which gives excellent results with biological materials like thyroid gland (ANALYST, 1932, **57**, 603), found to be entirely satisfactory when applied to these ointments. The following method was finally adopted and gave very consistent results:

About 2 g. of the well-mixed ointment are weighed in an open capsule, which may be prepared by cutting the bottom off a test-tube, a little powdered pumice is added, and the whole is dropped into 100 ml. of strong sulphuric

acid in a 400-ml. distilling flask connected with an air-condenser fitted with a bulb-tube dipping under 50 ml. of water in a tall cylinder. The distillation is then begun, heat being applied slowly at first. The distillate consists mainly of hydriodic and sulphurous acids. The contents of the flask are kept gently boiling for 3 to 4 hours, at the end of which time the whole of the iodine will have distilled. The condenser and delivery tube are rinsed through with cold water, and the distillate and washings are filtered to remove the small quantity of organic matter (fatty acids) which generally distils. Excess of nitric acid, followed by silver nitrate solution, is added, the mixture is heated to boiling, and the precipitate of silver iodide is collected in an alundum crucible,* washed, dried and weighed.

Since stainless iodine ointment contains neither free iodine nor potassium iodide, the methods of Evers and Elsdon† are not applicable to such preparations. The total iodine may, however, be determined by the method just described.

The ordinary and the stainless iodine ointments examined by us have contained one or more of the following substances in addition to iodine and, in most instances, potassium iodide:—paraffinum molle, arachis oil, lard, oleic acid, glycerin and parogen, the last being compounded from liquid paraffin, oleic acid, ammoniated alcohol and 90 per cent. alcohol.

In no case was any difficulty encountered. It is, however, possible that volatile iodine compounds, such as iodoform, would distil over partly unchanged, or even completely so. Other methods of dealing with such compounds must, therefore, be employed, and, in any case, ointments containing them do not comply with any formula for *iodine* ointment in the B.P. or the B.P.C. The purpose of the present note is merely to give a method of dealing with such preparations as may contain fatty or other substances capable of absorbing iodine.

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THE EXAMINATION OF RUBBED SPEARMINT

Spearmint (*Mentha viridis*) which has been dried and rubbed through sieves, is sold in considerable quantities in packet form for culinary use. The detection, in 1933, of the adulteration of foreign spearmint with the dried leaves of *Ailanthus glandulosa*[1] has resulted in increased attention being paid to the examination of dried spearmint. Stress has been laid upon the necessity of microscopic examination, and tentative limits have been suggested for ash and essential oil content.[2]

Some time ago we had occasion to examine a consignment of dried spearmint which had been rejected by another analyst. The mint was said to contain a small quantity of *Ailanthus*. Upon microscopic examination about 1 per cent. of striated cuticle, reminiscent of *Ailanthus* was found. This striated epidermis occurred only in very small fragments, and careful examination failed to reveal any of the characteristic hairs of *Ailanthus* or any calcium oxalate crystals. Moreover, when the specimens were compared under the microscope with *Ailanthus*, it was seen that there were differences in structure, although the resemblance was close.

In view of the facts that the spearmint in question was grown in Bedfordshire, the farm being open to inspection, and that no *Ailanthus* trees were in the vicinity,

* In the gravimetric determination of halides we have found alundum crucibles much more satisfactory than the ordinary Gooch type.

† Evers and Elsdon (*Analysis of Drugs and Chemicals*, 1929, p. 259) state that the stainless ointment should contain not more than 0·5 per cent. of free iodine when determined by their method.

it was concluded that some unidentified weed had contaminated the consignment. It was decided to investigate the matter further, and to this end some of the growing mint was plucked and dried in air in the laboratory, and the leaves were rubbed through a sieve. The rubbed leaves were prepared for examination by boiling for two minutes with 1 per cent. caustic potash, centrifuging and washing with water, followed by treatment with chloral hydrate solution. Finally, the leaves were washed in water and mounted in dilute glycerin. Upon microscopical examination the same striated epidermis was found to be present in an amount not exceeding 1 per cent. Further examination of the mint leaves showed that the striated cuticle came from an area at the base of the midrib.

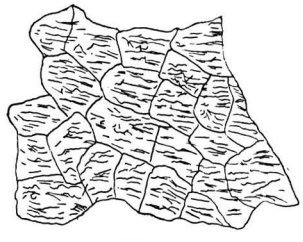

Fig. 1

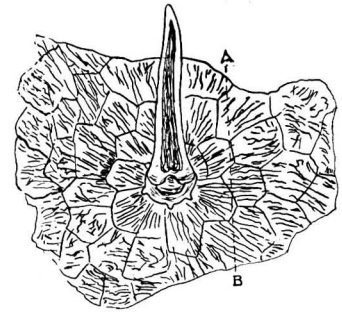

Fig. 2

A drawing (Fig. 1) of the structure was made with a Watson–Abbe eyepiece, and a drawing of the upper epidermis of *Ailanthus* is shown in Fig. 2. If a line be drawn from A to B on the *Ailanthus* picture (Fig. 2) and the area to the right compared with a similar area on Fig. 1, it will be seen that there is some similarity in the structure of the cells. During subsequent work on this subject it was found that the palisade ratio, suggested by Zörnig and Weiss,[3] and developed by Wallis and Dewar,[4] afforded another means for distinguishing *Ailanthus*.

In our experiments we found the palisade number for spearmint to be 5–7, whilst that of *Ailanthus* was 7–13. Measurement of the length of the stomata showed an upper limit of 30μ with an average of 24μ for spearmint, whilst *Ailanthus* stomata often reach 50μ.

It therefore follows that perfectly genuine spearmint may show a small proportion of striated epidermis somewhat resembling that of *Ailanthus*, but the presence of the latter should not be reported unless other diagnostic features are also present.

Our thanks are due to Mr. T. E. Wallis for helpful advice and to the directors of Messrs. Potter & Clarke, Ltd., for permission to publish this note.

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DETERMINATION OF THE CALCIUM AND PHOSPHATE CONTENT OF BONES

WITHIN the past two years a number of analyses of bones were made for the University of Pennsylvania Museum. These bones were specimens taken from excavations in Egypt, Central America and Alaska. Results and conclusions of this work, together with the work of other investigators, will be published later. This note presents a comparison of the results obtained by several analytical methods which were used in the analysis of standard solutions and bone solutions.

The chemical analysis of each sample of bone required the percentage of carbonate, calcium and phosphate. The carbonate-content was determined in the usual way by decomposing an air-dried sample of bone with hydrochloric acid. The carbon dioxide was absorbed in a Midvale absorption tube containing ascarite. The solution containing the calcium chloride and phosphoric acid was transferred from the digestion flask to a 500-ml. measuring flask and diluted to a known volume. Aliquot portions were used for the determinations.

A standard solution was prepared by dissolving a known amount of pure acid potassium phosphate, calcium carbonate and a trace of magnesium oxide in a small amount of hydrochloric acid and diluting to the mark in a 500-ml. measuring flask. This gave a solution similar in composition to that of the dissolved bones. Aliquot parts of this solution were used to test the methods.

DETERMINATION OF CALCIUM.—The commonly used basic acetate procedure[1] was tried and found to be unsatisfactory with only one precipitation. In order to obtain good results two precipitations were necessary. The most satisfactory method, alike for speed and accuracy, is that given by Hillebrand and Lundell.[2] The calcium is precipitated in the presence of the phosphate with an excess of oxalic acid and ammonium oxalate and filtered on to a Gooch crucible. The Gooch crucible containing the precipitate is transferred to a beaker and treated with sulphuric acid, and the liberated oxalic acid is titrated with standard potassium permanganate solution.

TABLE I

CALCIUM DETERMINATIONS

A. Standard Solution. B. Bone Solutions.

Percentage calcium (one precipitation)

	Basic acetate method	Oxalic acid and ammonium oxalate method	Calculated value
A.	19·54	20·15	20·17
	19·43	20·15	
B.	31·92	33·74	
	25·26	25·58	
	31·06	31·11	
	26·55	26·92	
	30·11	30·42	
	30·74	31·36	

Another standard solution containing 6·5 per cent. of magnesium was used to determine the accuracy of the oxalic acid and ammonium oxalate method. With one precipitation, in the presence of the higher percentage of magnesium, two determinations gave 18·87 and 18·86 per cent. of calcium. The calculated value was 18·63 per cent.

DETERMINATION OF PHOSPHORUS.—The phosphate was precipitated with an excess of ammonium molybdate.[3] The phosphomolybdate was dissolved in an

excess of standard (carbonate-free) sodium hydroxide solution. The excess of base was titrated with standard hydrochloric acid, phenolphthalein being used as indicator. Standardisations and titrations for each method were carried out under the same conditions. Results obtained from titration of the phosphomolybdate in the hot (80° C.), and in the cold (room temperature) are given in Table II.

TABLE II

PHOSPHATE DETERMINATIONS

A. Standard Solution. B. Bone Solutions.

Percentage of phosphate (PO_4).

	Hot titration	Cold titration	Calculated
A.	34·18	34·07	
	33·70	33·66	
	34·26	33·12	
	33·11	33·66	
	33·89	33·13	
Average	33·83	33·53	33·56
B.	43·29	42·12	
	35·16	34·96	
	35·87	34·10	
	44·50	43·50	
	42·55	42·06	
	39·72	38·30	

SUMMARY.—1. During an investigation of the chemical composition of specimen bones taken from recent excavations, it was necessary to check the accuracy of the volumetric methods used in the determination of calcium and phosphorus.

2. The basic acetate method for the determination of calcium in the presence of phosphorus was compared with the oxalic acid and ammonium oxalate method. With one precipitation the latter method gave excellent results for calcium, whereas the basic acetate method gave low results. In the presence of 6·5 per cent. of magnesium the oxalic acid and ammonium oxalate method gave high results, but these were within the limit of error for this type of work.

3. The precipitation of phosphorus as ammonium phosphomolybdate and titration with standard alkali gave high results when the titration was carried out in a hot solution. The end-point was more distinct in titrations made at room temperature.

The authors gratefully acknowledge a grant from the Faculty Research Committee of the University.

REFERENCES

1. Hillebrand and Lundell, *Applied Inorganic Analysis.* New York: John Wiley & Sons, Inc. 1929. Pp. 71, 72.
2. *Ibid.*, p. 501.
3. *Ibid.*, p. 568.

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DETECTION OF FORMALDEHYDE IN MILK

In testing for the presence of formaldehyde in milk by Hehner's method, trouble has occasionally been experienced, owing to the composition of present-day commercial sulphuric acid. This is probably due to the presence of sulphur dioxide, and, possibly, also of other impurities, introduced in the contact process, which were absent from acid obtained by the lead chamber process. It appears preferable, therefore, to use pure acid with the addition of a trace of a ferric salt and to carry out a control test with every delivery of acid. Acid which gives negative colour reactions may frequently be sensitised by the addition of a trace of potassium permanganate, but the sensitivity thus obtained is usually of a temporary nature only, and it is better, therefore, to discard such deliveries for use in this reaction.

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A SOUND-PROOF BOX FOR ELECTRICALLY-DRIVEN LABORATORY CENTRIFUGES

Owing to the rapid development of colorimetric and micro-methods of chemical analysis, many laboratories are now adopting methods in which centrifugal separations play an important part. The advantages of an electrically-driven centrifuge are obvious, but many have one very characteristic disadvantage, namely, they are noisy.

The noise set up by the concurrent use of two electrically-driven blood centrifuges standing* on a teak bench in these laboratories was of a high-pitched and piercing nature, and an attempt was made to find a method of eliminating this disturbance. Several of the simpler specifics were tried, including the mounting of the machine upon rubber and typewriter mats, soft asbestos and cotton-wool pads, but none of these proved very satisfactory. It was decided, therefore, that a sound-proof box would offer the only satisfactory remedy, and the writer's model, described below, was found to be almost sound-proof.

Construction of the Box.—A box just large enough† to accommodate the centrifuge was constructed of $\frac{3}{4}$″ deal boards. It was fitted with a lift-up lid, secured by hinges at the back and fastened by a bolt at the front. When open, the lid rested against the laboratory wall, but, where this is impracticable, a stay-hinge could be fitted.

The inside surfaces of the box were covered with rubber sponge mats,‡ faced on one side only with a thin solid layer of rubber. They were fixed by means of nails, so that the sponge surface was in contact with the wood. The bottom was completely covered with a 1″ thick mat, but, for all other surfaces, mats of $\frac{1}{2}$″ thickness were used. The side mats were cut so as to stand upon the bottom mat and to reach to within about $\frac{1}{4}$ inch of the top of the box, thus allowing the covered lid to close down tightly wood to wood, with its attached sponge mat (cut to the internal dimensions of the box) fitting snugly inside on to the tops of the side mats. The four corners were also plugged with 1″ × 1″ strips of the material, extending from the bottom mat to within about $\frac{1}{4}$ inch of the top of the box. A small hole was cut at the top of one side to allow the flex to pass through to the external electrical resistance. The centrifuge was lowered into the box and allowed to

* They were not screwed down, as in this and many laboratories portability is an important factor.

† The internal dimensions of the box were about 16″ × 16″ × 15″ high, in order to accommodate a machine 12½″ high by 12½″ diameter.

‡ Supplied, specially cut to size, by Messrs. Hellewell & Co., Liverpool.

rest upon the bottom mat. The machine must not be screwed down, nor must the metal safety bowl and lid be omitted. It will be noticed that the revolution counter cannot be used with the machine enclosed in the box, but the resistance slide may be easily calibrated occasionally to serve as a rough guide to the speed of the centrifuge.

The act of opening or closing the box in addition to the removal or replacement of the metal cover, as the case may be, may seem to be a rather tiresome procedure, but actually the habit becomes almost effortless after a short time. The portability of the equipment is in no way impaired if the electrical resistance is not fixed to the box, and the centrifuge can be moved in or out at will.

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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.

METROPOLITAN BOROUGH OF FULHAM

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

CHOCOLATE EASTER EGGS.—Four samples of chocolate Easter eggs were condemned on account of the presence of maize starch, two samples containing 10 per cent., and the other two 20 per cent. of this ingredient. The vendors claimed that the eggs were not labelled as chocolate, but such an explanation is of little value, since chocolate eggs were demanded, and there is no doubt that this type of product is sold to an unsuspecting public in the hope that it will be bought as chocolate.

COPPER IN TOMATO PURÉE.—Four samples of tomato purée were reported as adulterated on account of the presence of copper. Two samples contained 12 parts per million, whilst the other two contained 20 parts of copper, and 87 and 345 parts, respectively, of tin. These purées were all of Continental origin.

COMPOUND TINCTURE OF CARDAMOMS.—Three samples were found to be of B.P. 1914 quality, instead of conforming to the present Pharmacopoeia. The present preparation contains 60 per cent. of alcohol, as compared with 45 per cent. in the 1914 B.P., and, consequently, a larger proportion of active ingredients.

GREY POWDER CONTAINING TALC.—Two samples of grey powder were adulterated. One of these was deficient to the extent of 50 per cent. of mercury, and was compounded with talc instead of chalk; the other was 92 per cent. deficient in mercury.

THYROID TABLETS.—Four samples of thyroid tablets were submitted for examination. The samples were too small to permit of anything like a complete examination, but the quantities of iodine, calculated on the stated dose of thyroid present, which serve as a guide to the amounts of thyroxine, varied from 0·159 to 0·573 per cent. It was noted that only two of the samples were sold as being of pharmacopoeial quality, but it is unsafe to allow such a wide variation in the potency of active drugs. This variation can normally only be detected by the doctor through the effect he observes on the patient. It is to be hoped, therefore, that in future Pharmacopoeias it may be possible to give some other test which can be carried out on quantities which the normal purchaser would obtain.

T. MCLACHLAN

METROPOLITAN BOROUGH OF HAMMERSMITH

ANNUAL REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1934

PLACE OF ABSTRACTION OF FAT FROM MILK.—In one prosecution the Bench took the unique course of dismissing a summons on the ground that, although they were satisfied that the abstraction of fat certified had indeed taken place, yet they were not satisfied as to *where* it had taken place. They expressed the hope that the Council would take the matter further in order to settle the point. So far as I am aware, there is no precedent for such action.

"REAL" CREAM CONFECTIONERY.—Seven samples, out of a total of 11, of various types of cream confectionery were reported as adulterated on account of the use of cream substitutes as a filling material. Proceedings were instituted in respect of four samples, and convictions were obtained in each case, the total penalties inflicted amounting to £12 2s. The use of such terms as "cream buns" or "cream sponge sandwich" is calculated to deceive the purchaser, and it is a very debatable point as to how far the word "cream" can legitimately be employed in the generic, instead of the specific sense. There is no doubt, however, that most purchasers of this confectionery buy it under the impression that the cream filling really is cream. In the cases cited above the articles were sold as "*real* cream" buns, cakes, etc.; hence, there could be no two views as to whether deception was intended or not.

IODINE OINTMENT.—Of six samples of iodine ointment analysed during the year, no less than 5 were condemned. Two were ointments of a very different type, made from methyl salicylate (oil of wintergreen) and petroleum jelly, with the addition of a dark brown colouring matter to make them resemble iodine ointment. In the remaining three instances traces only of iodine or potassium iodide were present, whereas the British Pharmacopoeia of 1914, and the British Pharmaceutical Codex of 1923 and 1934, require four per cent. of each.

F. W. EDWARDS

CITY AND COUNTY OF KINGSTON-UPON-HULL

ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEAR 1934

OF the total number of samples of food and drugs examined during the year, 1229 were official and 664 informal samples.

DIRT IN MILK.—During the year only 7 of 1112 samples of milk (0·6 per cent.) showed an appreciable amount of visible dirt in the ordinary one-third pint samples. This contrasts favourably with the condition in 1925, when 10·4 per cent. of the samples were dirty.

When one of these ordinary-sized samples is found to contain appreciable amounts of visible dirt (which is detected by allowing the milk to remain at rest for one–two hours in its original bottle in a sloping position, by which means the dirt is largely concentrated in a small area at the bottom of the bottle), the fact is reported to the Sampling Officers of the Health Department, and as soon as practicable a larger sample (3 pints, divided into three one-pint samples) is obtained with special precautions, when the amount and character of the dirt (if any) can be ascertained with some accuracy on the larger sample then available for analysis.

The Milk and Dairies Order, 1926, enjoins cleanliness on the cowkeeper, without giving the local authority any real means of determining whether the milk has been produced by such cowkeeper under the conditions laid down in the Order.

It is contended by the writer that milk which can be proved by analysis to be dirty (that is, to contain on examination by a standard method more than two parts of moist extraneous matters in 100,000 parts of the milk, such extraneous matters consisting partly or largely of *dung*) has certainly not been produced under the conditions laid down in the Order quoted, and that evidence that milk is so contaminated should be sufficient to obtain the conviction of the producer in the Courts. Many convictions have been obtained by the Corporation under the Sale of Food and Drugs Act, but a local authority would be in a much stronger position if a standard of chemical cleanliness were definitely laid down under the Milk and Dairies Order, 1926. An attempt was made to secure the inclusion of the desired clause in the Draft Order as first issued, but it was unsuccessful.

CREAM BISCUITS.—One of 7 samples of biscuits examined attracted special attention, since it was labelled "Dairy Cream Biscuits"—a description which it was thought entitled a purchaser to expect some proportion of real cream as an ingredient of these biscuits. About three-quarters of the weight of the biscuits was actual farinaceous material, with one-quarter as a "paste" consisting of three parts of sugar with one part of fat. The fat contained at least 95 per cent. of a vegetable fat of the nature of coconut fat, with not more than 5 per cent. of butter-fat. This analysis showed that the name applied to this product was unjustified, and the makers finally agreed to alter the name, omitting the offending word. Any regulations made by the Ministry of Health on standards and definitions for foods should include products such as these so-called "cream" biscuits.

POTTED MEATS.—Ten of 26 samples of potted meat were reported as adulterated. They contained, respectively, 3·5, 4·0, 7·5, 2·3, 4·8, and 5·7 per cent. of moist farinaceous material (mainly wheat flour); 5·2 per cent. excess water and 500 parts per million of boric acid; 5 per cent. excess water and 400 parts per million of boric acid; 3·0 and 6·2 per cent. excess water. The standards of composition adopted by the Corporation include a maximum of 70 per cent. of water, and freedom from foreign farinaceous ingredients.

SULPHUR GASES IN THE AIR.—The daily determinations of the total amount of sulphur gases in the air of the city have been continued throughout the year under review, and the following are the results obtained. These figures for sulphur gases follow those for total pollution in the central area, and show a diminution compared with the previous year.

SULPHUR ACIDS IN THE AIR (CITY OF HULL)

(in terms of sulphur dioxide, volumes per million)

1934 Month	Daily maximum	Daily minimum	Daily average
January	0·237	0·025	0·108
February	0·234	0·050	0·110
March	0·200	0·027	0·079
April	0·113	0·027	0·069
May	0·077	0·019	0·045
June	0·092	0·016	0·043
July	0·053	0·010	0·025
August	0·059	0·013	0·028
September	0·065	0·012	0·031
October	0·117	0·027	0·065
November	0·224	0·050	0·118
December	0·142	0·022	0·068

A. R. TANKARD

Legal Notes

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

CHOCOLATE ROLL DEFICIENT IN CHOCOLATE

On August 17th, at Aylesbury Petty Sessions, a London wholesale firm of bakers and confectioners was summoned for wilfully giving, with an article of food, namely, a chocolate Swiss roll, a label which falsely described the article sold, and also with giving a false warranty contrary to Section 30 of the Food and Drugs (Adulteration) Act, 1928. Mr. C. B. Guthrie, barrister, instructed by the solicitors of the London Master Bakers' and Confectioners' Protection Society, pleaded not guilty to both charges.

Outlining the case for the prosecution, Mr. S. E. Wilkins stated that an Inspector of the county purchased a chocolate roll for analysis, and, in consequence of the report received, the Inspector, at a later date, took a further sample on delivery at the retailer's premises. The report from the Public Analyst was as follows:—"The sample is not genuine, being artificially coloured to resemble chocolate." Under the heading of observations it stated, "The amount of chocolate present, if any, is negligible, being less than one per cent."

The roll purchased was in a cardboard carton marked " . . . finest quality Swiss Roll. Is made of the finest quality flour." At each end was marked, " . . . 6d. Swiss Roll chocolate." The roll inside was wrapped in grease-proof paper marked, " . . . chocolate roll—purity guaranteed. Made from the finest quality ingredients; made in a model bakery under ideal conditions. 6d."

Mr. Wilkins informed the Bench that there was no standard fixed for chocolate roll or cake, but there was ample authority that, if there be no standard, the justices must fix one on the evidence. There need not necessarily be a quantitative standard, but there might be a minimum standard.

When the rolls were delivered to the retailer an invoice was handed to him showing them to be "balance of order," and at the bottom of that invoice was a guarantee as follows:—"We guarantee all foods supplied by us to be of the nature, substance and quality described, and to comply with the provisions of the Sale of Food and Drugs Act, 1928, and with all other statutory requirements or regulations relating to the sale of food."

Mr. Eric Voelcker, F.I.C., one of the Public Analysts for Buckinghamshire, referred to analysing the samples and to issuing the certificates. In cross-examination the witness suggested that not less than 4 per cent. of dry fat-free cocoa material should be used to give the proper flavour and taste and to justify the description "chocolate." In reply to Mr. Wilkins, witness said that the sample did not taste of cocoa at all. The colouring matter should not take the place of the ingredient which was necessary. It should be chocolate in nature and not in colour.

Mr. T. Macara, F.I.C., supported the views of the previous witness, and said that if an article was described as "Chocolate Swiss Roll," there should be sufficient cocoa powder to give it both the colour and flavour of chocolate. From his own observations he would say that about 4 per cent. of non-fatty coçoa material was required to give a chocolate flavour. An article with less than 1 per cent. would not have the flavour or colour of chocolate.

Mr. Guthrie submitted that in law both summonses must fail. Dealing with the alleged false warranty, he submitted that there must be a warranty in writing

delivered when the contract of sale had been completed, and the warranty relied on in this case was a so-called guarantee at the foot of the invoice which accompanied the goods when delivered, and was not a warranty within the meaning of the section of the Act under which these proceedings had been taken. The goods must be sold with the warranty, but the retailer had had the contract of sale some days before the goods had been delivered. The invoice was not a contract of sale. With regard to the other summons, Mr. Guthrie referred to Section 18 of the Act, and submitted that the officials of the county had failed to comply with the procedure of the Act. In reply, Mr. Wilkins submitted that the warranty was in order and that the purchase was not completed until the delivery of the goods. Regarding the other summons, he stated that they were not dealing with Section 18, but with Section 16 of the Act, which provided that a sample may be taken at the time of delivery.

There was considerable discussion of the points raised, and, after a short retirement, the Bench upheld the objection of the defence regarding the false warranty, but were of the opinion that the prosecution were acting, in the other summons, under Section 16 of the Act, and, therefore, complied with the law.

In submitting the case for the defence, Mr. Guthrie said that these rolls did not purport to be chocolate cake—they were not sold as such. Nobody buying them expected chocolate cake, but merely rolls with a chocolate flavour. The word "chocolate" was used to differentiate these rolls from those of other flavours.

The managing director of the firm said that they used 1·03 per cent. of cocoa powder, and had used this amount since 1926. Approximately 16,000 chocolate rolls were made each week, and no complaint had ever been received from the public.

Evidence was also given by the president and a past-president of the London Master Bakers' and Confectioners' Protection Society that the amount of cocoa powder used was a reasonable proportion, although, personally they used a little more.

The Chairman announced that, in respect of the dismissed summons, costs of three guineas would be allowed to defendants. In respect of the summons for a false description they had decided to convict. Evidence for the defence showed that something like 2 or 3 per cent. of cocoa powder was a reasonable amount to use. They would inflict a penalty of £3 and costs amounting to £14 5s.

Department of Scientific and Industrial Research

Food Investigation

THE REFRIGERATED GAS-STORAGE OF APPLES*

THIS leaflet deals with the process in which control of the composition of the atmosphere in the store is the principal feature. The outstanding advantage of gas-storage is that ripening of the fruit is slowed down to about half the rate in air at the same temperature. Carbon dioxide has the specific effect of retarding the change of the green colour of the fruit to yellow, and also preserves the hardness of the fruit almost unchanged. The surface-eating Tortrix larvae are quickly killed in gas-storage.

Directions are given for the pre-treatment of fruit before storage, for the interval to be allowed between gathering and storage, and for the time for unloading the store.

* Leaflet No. 6. By F. Kidd, M.A., D.Sc., and C. West, M.A., D.Sc. Obtainable gratis on application to the Secretary, Department of Scientific and Industrial Research, 16, Old Queen Street, Westminster, S.W.1.

There are also sections dealing with the size of the chamber, the methods of making the chamber gas-tight, and of obtaining the correct atmosphere in the store. In this connection it is pointed out that the rate at which carbon dioxide is produced is dependent upon the temperature; for instance, apples produce approximately twice as much carbon dioxide at 60° F. as at 40° F. Control of carbon dioxide and of oxygen by restricted and regulated ventilation alone will provide the required atmosphere only when the concentrations of the two gases add up to 21 per cent. Chemical absorption of the oxygen can be controlled, either by regulated circulation of the atmosphere of the chamber over a large quantity of absorbent, or by introducing limited charges of the absorbent into the chamber at intervals as required.

The following table gives the temperatures and atmospheres recommended for the storage of home-grown apples.*

Variety	Temperature† °F.	Carbon dioxide Per Cent.	Oxygen Per Cent.
Culinary Varieties—			
Annie Elizabeth ..	34 to 35	0	21 (air)
Bramley's Seedling ..	40	8 to 10	13 to 11‡
King Edward VII ..	37 to 40	5 to 10	2·5
Lane's Prince Albert..	39 to 40	5	2·5 to 5
Lord Derby	40	8 to 10	13 to 11‡
Monarch	34	5	2·5 to 5
Newton Wonder ..	34	0	21 (air)
Stirling Castle ..	40	8 to 10	13 to 11‡
Dessert Varieties—			
Blenheim Orange ..	37 to 38	0	21 (air)
Cox's Orange Pippin	39 to 40	5	2·5
Ellison's Orange ..	34	5	2·5 to 5
King Pippin	39 to 40	0	21 (air)
Laxton's Superb ..	40	10	2·5
Worcester Pearmain	34 to 35	5	2·5 to 5

The humidity of the atmosphere in gas-stores for apples has so far presented no difficulty in practice. Under commercial conditions it varies between 85 and 98 per cent. of saturation. The relative humidity of the atmosphere actually surrounding the fruit is the main factor determining the rate at which it loses water.

There is now much evidence that the accumulation of volatile substances produced by the fruit is harmful, and may cause superficial scald. It has been found in practice that when ripening fruit is placed in gas-storage with unripe, green fruit, damage is caused to the latter, even when oiled wrappers are used.

The capacity of the refrigerating plant should be sufficient to reduce the temperature of the fruit from 65° F. to 40° F., with an external temperature of 70° F., within 4 to 5 days after the chamber is closed.

The leaflet concludes with a description of the most suitable boxes for fruit and of methods of stacking in the store, and of the thermometers and instruments used for indicating the composition of the atmosphere. There is also a list of scientific references and an appendix on the cost of gas-storage.

* It should be noted that a few varieties keep best in ordinary cold storage. Amongst these are the two varieties that are particularly susceptible to superficial scald, *viz.* Newton Wonder and Annie Elizabeth.

† Temperature of flesh of apple.

‡ Atmospheres obtainable by controlled ventilation, as practised in commercial gas-storage.

Government of Madras

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1934

IN his annual report Dr. Clive Newcomb states that 1553 cases were investigated during the year, as compared with 1518 in 1933. The total number of human poisoning cases was 327, poison being detected in 174. Oleander heads the list of poisons with 41 cases, opium or its alkaloids come next with 24 cases, closely followed by datura or mydriatic alkaloids with 23 cases. Several of the cases present points of analytical interest.

MERCURIC CHLORIDE POISONING.—In one case a man was given poisoned milk and died four days later. In the vomit 25 grains of corrosive sublimate were found, but the visceral matter contained only traces of mercury. In another case (suicide), in which a man confessed to having swallowed mercuric chloride in coffee, death occurred about a fortnight later; only extremely minute quantities of mercury were present in the viscera. On the other hand, in two cases in which death was very rapid large quantities of mercury (30 and 50 grains) were found in the viscera. Thus, in fatal cases of mercuric chloride poisoning, if the victim lives for some time after taking the poison, only very small amounts of mercury may be found in the viscera.

Analytical Notes on the Determination of Mercury in Viscera.—(*Cf.* p. 734.)

MADAR JUICE POISONING.—There were two cases of death from drinking madar juice. From the viscera in each case extracts giving the reactions described in my Annual Report for 1933 (ANALYST, 1934, **59**, 542) were obtained.

Ester Test for Madar Juice.—The sulphuric acid method of esterification of madar juice often yields a liquid the odour of which is masked to a large extent by the odour of sulphur dioxide, ether, etc. We found that the ester test for madar juice could be more conveniently made in the following manner:—The material, rendered slightly alkaline and dried, is extracted with alcohol, and the solution is esterified by passing dry hydrogen chloride gas through the alcoholic solution. Then a solution of potassium hydroxide is added to neutralise the hydrochloric acid while the contents are kept cool. If madar juice was present in the original material, the liquid now exhibits a pleasant odour strongly resembling that of fresh ripe strawberries. This test can be carried out even with small quantities in a test-tube. If desired, the neutralised solution can be distilled to obtain the ester or esters.

OLEANDER POISONING.—Thirty-six of the 41 cases in which oleander was detected were fatal. The symptoms of oleander poisoning, so far as can be gathered from the histories furnished, appear to be tingling of tongue, shivering of hands and feet, and, later, of the body, epigastric pain, vomiting, in a few cases purging, rapidity and failure of pulse, and asphyxial symptoms. In some cases convulsions also occurred. Unconsciousness set in only towards the end.

The post-mortem examination showed that in about half of the fatal cases the heart was contracted and all its chambers empty. In about a third of the cases the right side of the heart was filled with dark blood and the left side of the heart was empty. In practically all the cases the lungs were congested. There was also congestion of liver, spleen, kidneys, and brain in most of the cases, and the stomach and intestines showed patches of congestion.

The cases were mostly suicidal, and it seems as if oleander were taking the place of opium as the poison of choice for suicide.

GLORIOSA SUPERBA POISONING.—A man of 45 committed suicide by eating the root of *Gloriosa superba*. From the viscera a poisonous extract similar to that

from the root was obtained. It was found that neither the acid nor the alkaline ethereal extract obtained in the extraction of the root by the Stas-Otto process was fatal to frogs, but, on adding ether to an alcoholic (rectified spirit) extract, a whitish precipitate was obtained, which, when separated and injected into frogs, killed them. The precipitate was freely soluble in water, but insoluble in absolute alcohol, ether, chloroform or amyl alcohol. Yellow oleander seeds, when treated in the same manner, yielded a similar poisonous precipitate which, however, was soluble in absolute alcohol as well as in amyl alcohol. Further, the precipitate from yellow oleander seeds yielded a blue colour on boiling with dilute hydrochloric acid (*cf.* Annual Report for 1932). The precipitate from *Gloriosa superba* did not give any colour with hydrochloric acid. Moreover, yellow oleander seeds in addition yield an acid ether extract poisonous to frogs and giving a purple colour with concentrated sulphuric acid. The poisonous extract from *Gloriosa superba*, obtained as described above, appears to be a glucoside. Its further nature is under investigation.

The microscopic examination of *Gloriosa superba* root revealed: (1) An epidermal tissue of elongated cells containing minute, perfectly spherical bodies, all nearly of the same size, about three to four $m\mu$ in diameter, many of them having crenated edges and radiating striæ. These curious bodies are not destroyed by boiling the tissue in water, in chloral hydrate solution, or in hydrochloric acid, but appear to be soluble in potassium hydroxide solution; (2) a parenchymatous tissue of thin-walled polygonal cells closely packed with starch granules. The starch granules consist mostly of ovoid grains, with some spherical, semi-spherical and semi-elliptical grains. There is a well-marked hilum in each granule, and there are distinct concentric striations. The hilum is situated at the *broader* end of the ovoid granules at a distance of about a third of its diameter. The average diameter of most of the grains is about $35m\mu$. There are, however, a few grains with diameters of $15m\mu$, and some with diameters of $45m\mu$. In some of the spherical grains the hilum is in the centre of the grain. The starch grains of *Gloriosa superba* differ from those of potato starch in the fact that in potato we find much larger grains (70 to $110m\mu$ in diameter), and the hilum in potato starch is found close to the *narrow* end of the grain. Spiral vessels and bast fibres are rather scarce.

Cannabis indica Poisoning.—A father was suspected of having poisoned his son. There were no definite post-mortem signs, as the body was decomposed. The suspected poison—a powder—was also sent. The suspected poison was found to be the powdered leaf of Indian hemp, and we obtained from the stomach a poisonous extract which gave a positive Beam's test with alcoholic hydrochloric acid. The other Beam's test, *viz.* the formation of a purple colour on addition of alcoholic potash to a petroleum spirit extract of the substance and evaporation at room temperature, was negative, and this test does not work satisfactorily in our hands, even with some known specimens of Indian hemp leaf. We were, however, not absolutely certain of the presence of Indian hemp, as we could not get any sediment resembling Indian hemp under the microscope. There have been fatal cases of poisoning by Indian hemp, both accidental and suicidal, and cases have also been reported where the drug appears to have been used for the purpose of facilitating the commission of an offence, but this is the first fatal homicidal case we have met.

Karu Veerathalai Leaves (*Elaeodendron glaucum*, Pers.).—We examined last year a case of poisoning caused by drinking a decoction of the leaves of this plant. The symptoms were not stated. At the post-mortem examination the heart cavities were found to be empty. The lungs were soft and slate coloured; the stomach and intestines were congested with a thick yellow liquid in the latter, and the membranes of the brain were vascular. We obtained from the stomach a poisonous resin similar to the poisonous extract obtained from the leaves and bark

of *Elaeodendron glaucum*. This plant is a shrub occurring in the hotter parts of India. In *Watt's Dictionary of the Economic Products of India* it is stated that the root is a "specific" against snake bite (whether internally or externally is not stated). The bark is said to be used in native medicine and to be a virulent poison, and the leaves to be used as a fumigant to rouse women from hysterical fits. The leaves and bark were examined in this laboratory, and both yielded a poisonous resin which gave, in chloroformic solution, with acetic anhydride and sulphuric acid a green colour (Liebermann reaction). The resin was found to be freely soluble in chloroform and sparingly soluble in ether and in petroleum spirit.

Jammi Leaves (*Prosopis spicigera* L.).—Samples of leaves received were said to have been used in a suspected poisoning case, but we did not detect poison in the viscera. The leaves examined here gave a poisonous acid ethereal extract which did not give the Liebermann reaction for resin. It gave a brown colour when dissolved in acetic acid containing ferric sulphate, and floated on sulphuric acid containing a trace of iron (Keller's reaction). The extract did not reduce Fehling's solution.

Picrotoxin Poisoning.— A woman was found at bed-time to be suffering from pain in the stomach, with vomiting and convulsions. She died at about 4 a.m. the next day. The viscera were sent to us, but we had no information as to the nature of the poison swallowed. We obtained from the viscera an acid ethereal extract which (1) was crystalline, (2) reduced Fehling's solution, (3) killed a frog with convulsions, (4) gave a brick-red colour on treatment with potassium nitrate and concentrated sulphuric acid followed by solid potassium hydroxide, and (5) gave a bright red colour on treatment with a solution of benzaldehyde in absolute alcohol followed by the addition of concentrated sulphuric acid. We did not obtain any alkaloid from the viscera. We therefore concluded that the acid ethereal extract we had obtained was picrotoxin, the active principle of *Cocculus indicus*.

Aconitine Poisoning.—Three children were given a decoction of some root with castor oil. They became restless and developed tingling of the lips and tongue, burning sensation in the stomach, with numbness in the body and inability to walk. Two of them died. From the stomach of one of the victims we obtained aconitine, but could not find any in the stomach of the other. There is little doubt that both died of aconite poisoning. Our inability to find it is noteworthy as showing how difficult it may be to find it in the stomach, even when the patient has been poisoned by it.

Identification of Gunpowder Carbon in the Tissues.—A man was alleged to have been shot with a gun. There was an injury in the neck which might have been due to a gun-shot wound. The gun, we were told, was loaded with country gunpowder and pebbles, no leaden bullet or shot having been used. The tissues around the wound were sent to us for examination to ascertain whether the wound was caused by gun-shot. As an examination of the tissues for lead would have been of no use in this case, we digested portions of the tissues (1) in cold nitric acid and (2) in cold hydrochloric acid plus potassium chlorate. After the tissues had dissolved, a fine black deposit of carbon was seen at the bottom in each case, showing that carbon had been embedded in the tissues. Sections of the tissue examined under the microscope also showed black foreign particles. The detection of elementary carbon imbedded in the tissues of the wound suggested that the tissues had been subjected to the explosion of a black powder at close range.

Identification of Typewriters.—Several cases requiring the identification of the machine on which a document had been typed were investigated, and the method outlined in my previous reports (Analyst, 1934, **59**, 39, 544) was used with conclusive results.

Medical Research Council
(Privy Council)

THE DETERMINATION OF IODINE IN BIOLOGICAL SUBSTANCES*

THE work described in this Report was undertaken because it appeared that the methods commonly in use for the determination of minute amounts of iodine in the presence of organic matter were unsatisfactory. Stress is laid upon the point that precautions must be taken to ensure that the atmosphere of the laboratory cannot become contaminated from outside sources (*e.g.* by the use of iodine in an adjoining room). Failure to obtain low and constant "blanks" is a sure indication of adventitious contamination.

From a study of the colorimetric and volumetric processes, the conclusion is drawn that the personal error in matching colour is undoubtedly greater than in judging the end-point of titration in the volumetric process. On the other hand, with the volumetric method, it must be fully appreciated that the figure obtained by titration measures the oxidising power of the solution. In the presence of oxidising agents other than iodic acid (chlorine, bromine, bromate, iron, vanadium, etc.), the figure obtained is not a true measure of the iodine originally present. Furthermore, in the presence of certain substances (nitrite, bromide, organic matter), the iodic acid may be partly reduced, when the results will be low. In spite of these defects, however, experience has shown that, when due regard is paid to its limitations, the volumetric process is to be preferred as a standardised method, owing to its comparative freedom from personal error.

The titrations are carried out with $N/500$ thiosulphate solution, a micro-pipette or burette being used. Soluble arrowroot starch has been found to be the most suitable indicator. For the oxidation of the iodide to iodate bromine water is preferable to chlorine water, and the conditions under which hydriodic acid is quantitatively oxidised by bromine have been thoroughly examined. A carefully standardised method has been based on the results of the study of the various processes, including the extraction of the iodide, and the destruction of the organic matter under varying conditions.

Tables of results obtained by the standard method in experiments in which known quantities (in γ) were added to milk powder, milk, hay and blood, are given in full, and these are followed by a detailed description of the standard method, and of modifications thereof for use with milk, vegetable materials, and other materials (oils and fats, drinking water, waters containing nitrates, materials containing sulphates or other sulphur compounds, fish products, saline materials, and organic materials) containing relatively very little iodine.

There is a final section on precautions to be taken and sources of error, and the Report concludes with appendices on the preparation of soluble arrowroot starch and on the electrolytic preparation of iodine-free potassium hydroxide, and a bibliography of selected papers bearing on the subject.

* Special Report, Series No. 201. By C. O. Harvey, B.Sc., A.I.C. Pp. 43. London: H.M. Stationery Office, Adastral House, Kingsway, W.C. August, 1935. Price 1s. net.

Ministry of Health

MILK PASTEURISING PLANTS

CIRCULAR 1473*

THE following circular has been issued to the Clerks of Local Authorities:

SIR,

1. I am directed by the Minister of Health to state, for the information of the Council, that he has recently published a Report by one of the Medical Officers of the Ministry on the Supervision of Milk Pasteurising Plants.†

2. The value of efficient pasteurisation in making milk safe for human consumption has become increasingly recognised during recent years, and was referred to with approval in the report of the Committee of the Economic Advisory Council on Cattle Diseases (Cmd. 4591); but if pasteurisation is to be effective in destroying the tubercle bacillus and other pathogenic organisms which may be present in milk, it is necessary that the process should be efficiently carried out.

3. At the present time, as the Council are aware, all milk sold under the designation "Pasteurised" is required to have been treated in the manner prescribed in Part IV of the Third Schedule to the Milk (Special Designations) Order, 1923, *i.e.* it must be retained at a temperature of not less than 145 degrees and not more than 150 degrees Fahrenheit for at least half an hour, and be immediately cooled to a temperature of not more than 55 degrees Fahrenheit. These requirements can be met with certainty only by what is known as "positive holding" (or the "holder method") by which the whole of the milk is retained or "held" at the required pasteurising temperature for the specified time.

4. There is evidence that some pasteurising plants at present in operation are imperfect in design or construction, or are not properly operated and controlled, with the result that efficient pasteurisation of the milk is not secured. The purpose of the present Report, as stated in the prefatory note, is to supply information on the subject of pasteurising plants, to explain the considerations involved in their construction, operation and cleaning, and to give some account of the appliances and methods employed in the subsidiary processes of bottle-washing and bottle-filling.

5. I am to remind the Council that one of the conditions subject to which licences for selling milk as "Pasteurised" may be granted is that the type of apparatus used for pasteurising and the methods employed shall be such as are satisfactory to the licensing authority. It is hoped that the Report will be of material assistance to officers of local authorities in reporting on applications for licences in respect of establishments at which the process of pasteurisation is proposed to be carried on, and in enabling those officers to exercise adequate supervision of pasteurising plants in respect of which a licence has been granted. With this end in view it is important that the Council should supply each of these officers with a copy of the Report.

6. A copy of this Circular is being sent to the Medical Officer of Health, and a copy of the Report is being sent to the Medical Officers of Health of those Authorities who are known to have issued licences in respect of pasteurising establishments. Further copies of the Circular and Report may be purchased through any bookseller or directly from His Majesty's Stationery Office.

I am, Sir,

Your obedient servant,

(*Signed*) A. K. MACLACHLAN

(Assistant Secretary)

May 16th, 1935.

* H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. Price 1d. net.

† Report on the Supervision of Milk Pasteurising Plants by Sir Weldon Dalrymple-Champneys, Bt., M.A., D.M., F.R.C.P. (Public Health and Medical Subjects, No. 77, Price 1s. 3d.).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Chlorine in the Fat of Flour. V. E. Munsey. (*J.A.O.A.C.*, 1935, **18**, 497–502.)—The bleaching of flour by a mixture of chlorine and nitrosyl chloride (Beta Chlora process), by chlorine alone, or by nitrogen trichloride (Agene process) increases the chlorine-content of the flour-fat. The Agene process adds only a small amount, but the Beta Chlora and chlorine processes add comparatively large quantities. The procedure recommended for determining the chlorine-content of the fat varies according as a green flame is or is not obtained when a little of the fat is heated on a copper wire. The most suitable solvent found for extracting the fat is aviation petrol, and the conversion of the chlorine in the extracted fat into the ionic form is effected by incineration.

For flour fats containing relatively little chlorine, the method given for the determination is virtually that described by Kent-Jones and Herd (Abst., ANALYST, 1930, **55**, 394), the result obtained being corrected by that of a blank determination with the reagents. For 28 unbleached flours examined in this way, the chlorine-content of the fat ranged from 0·4 to 1·8 p.p.m., the mean being 1·28. For unbleached rye flour the highest value found was 0·6, and the average 0·44 p.p.m. With Agene-bleached flours, the results varied from 2·5 to 13·7 p.p.m.

With flours bleached by the Beta Chlora or chlorine method, 75 g. of the flour are extracted with 150 ml. of aviation petrol, and the final determination of the chlorine may be carried out either gravimetrically as silver chloride or by the Volhard volumetric method. Details of the procedure are given. For 12 samples bleached by one of these two processes, chlorine-contents of 47·4 to 381 p.p.m. were found in the fats. T. H. P.

Transmission of Light through Eggshell. J. W. Givens, H. J. Almquist and E. L. R. Stokstad. (*Ind. Eng. Chem.*, 1935, **27**, 972–973.)—The visibility of the yolk-shadow in the commercial grading of eggs by "candling" will depend on any property of the shell which can control the passage of light through it. Tests were made on the transmission of light through eggshell in relation to thickness, water-content and protein-content. Water-content of the shell, determined by loss of weight when dried for 7 days *in vacuo* over phosphorus pentoxide at room temperature, was found to be the chief factor affecting light transmission, a sample with 1·8 per cent. of water giving a much higher transmission value than one with 0·9 per cent. The effect of water is probably due to the filling-in of the air-spaces between the calcite crystals in the shell with a medium of higher refractive index. Protein-content was found to be next in importance, the larger amounts of protein rendering the shell more opaque. Thickness of shell, and also the membranes present, had a minor effect on light-transmission. The two factors, *viz.* water and protein-content, are, as far as present knowledge indicates, independent of the true condition of eggs.

S. G. C.

Separation of Products resulting from the Enzymic Hydrolysis of Starch. J. L. Baker and H. F. E. Hulton. (*J. Inst. Brewing*, 1935, **41**, 375–377.)—The use of alcohol for the separation of the conversion-products of starch is criticised. The bulk of the maltose, the principal sugar present, can easily be isolated and obtained in the crystalline state, but the non-crystallisable substances (*e.g.* dextrins) present difficulties, as maltose adheres to them mechanically and, according to some workers, even forms compounds of the malto-dextrin series (*cf.* Ling and Baker, *id.*, 1897, 287). The practice of designating a particular material in terms of its solubility, or otherwise, in alcohol of a particular strength is inaccurate, because the process of separation involves pouring gradually a syrupy solution of the material in water into alcohol of known strength. The concentration of the alcohol, therefore, decreases gradually during this operation, owing to the addition of water, so that (*e.g.*) a fraction said to be insoluble in 89·3 per cent. alcohol may really be a mixture of fractions insoluble in alcohol over a range of strengths which vary from 96 to 89·3 per cent. This criticism applies only to substances produced by the enzymic hydrolysis of starch by malt between room-temperature and 70° C. When barley diastase acts on starch paste the reaction is simple, about 60 per cent. of maltose and 40 per cent. of α-amylo-dextrin being formed (*cf.* Baker, *id.*, 1902, 628), which may be separated almost quantitatively by the conventional method, because the latter is insoluble in alcohol, so long as the strength is 80 per cent. or over. Numerous variations in the technique of the alcohol method and in the nature of the precipitating solvent have proved discouraging, but it is considered possible to eliminate the difficulty by adding rapidly to a certain volume of a solution of the conversion products in water, such a volume of 99 per cent. alcohol that the strength of the resulting alcohol of any desired value. In one experiment 800 ml. of 99 per cent. alcohol were added rapidly to 400 ml. of conversion products (containing 93 g. of total solids, and produced by the action of isolated malt diastase on potato starch paste for 1 hour at 130° F.). The mixture was shaken well, the final strength of the alcohol being 66 per cent. The $[\alpha]_{D3\cdot93}$ of the insoluble portion was 178·3 (original value, 152·3). The dextrin was dissolved in water, and alcohol was added so as to produce again an ultimate strength of 66 per cent., the $[\alpha]_{D3\cdot93}$ being then 185·5, and after a further similar treatment, 186·4. In this way it is possible in a relatively short time to obtain a dextrin similar in physical properties to the "stable dextrin" of Brown and Millar (*id.*, 1899, 461). J. G.

Comparison of Commercial Pectins. C. J. Van der Bie. (*Chem. Weekblad*, 1935, **32**, 557–558.)—The following determinations were made on (*a*) a Californian citrus pectin; (*b*) and (*c*) two commercial citrus pectins from New York; (*d*) a German apple pectin; and (*e*) a slow-setting German pectin. *Methyl Alcohol.*—The material is saponified with warm alkali and acidified and distilled, the methyl alcohol in the distillate being oxidised to formaldehyde and determined colorimetrically with the Denigès fuchsin-sulphite reagent (*cf.* Von Fellenberg, *Biochem. Z.*, 1927, **85**, 69). *Calcium Pectate.*—The material is saponified in the cold with sodium hydroxide solution, and the precipitate produced on addition of calcium chloride solution in the presence of acetic acid and heating

is removed by filtration, washed, dried and weighed (*cf.* Mehlitz, *Koll. Z.*, **1927**, **41**, 132). *Carbon Dioxide* is determined by heating the sample for 8 hours with 12 per cent. hydrochloric acid in a stream of air (free from carbon dioxide), the gas being absorbed in a known quantity of barium hydroxide solution, the excess of which is back-titrated with hydrochloric acid in the presence of an excess of barium chloride (*cf.* Baker, *infra*). *Setting-power.*—A mixture of 2 g. of the sample and 200 g. of sugar is added to a boiling mixture of 200 ml. of water and 20 ml. of 0·1 *N* tartaric acid in an aluminium pan, and the whole mixture is gently heated until the weight is 288 g., and allowed to set. The breaking-strength of the gel is determined by measuring, on a water-manometer, the pressure required to insert a plunger below the surface. Other determinations made were of ash, yield of furfural phloroglucide (Tollens), the relative viscosity at 27° C. of a 0·75 per cent. solution in water, the *p*H value (as determined by the Wulff strip method), and the acidity (titration of 10 ml. of a 0·75 per cent. solution with 1·075 *N* sodium hydroxide solution, phenolphthalein being used as indicator). The results are tabulated, the extreme values in each case being (in percentages), ash, 1·75 for (*e*) to 11·65 for (*a*); furfural phloroglucide, 19·5 to 37·05; methyl alcohol, 3·1 to 10·8; calcium pectate, 47·9 to 92·4; carbon dioxide, 10·90 to 19·0; viscosity, 1·71 to 3·82, although sample (*e*) gave the exceptionally high figure of 6·59 (see below); *p*H value, 2·8 to 4·2; acidity, 0·50 to 1·32 ml. The setting powers followed the decreasing order, (*a*), (*b*), (*e*), (*d*), and (*c*). The reasons for the slow-setting properties of (*e*) were investigated further, and the high viscosity was held to be responsible. However, (*e*) gave no colour with iodine and potassium iodide solution, and, although it contained more glucose than (*b*), addition of 0·5 per cent. of glucose to a solution of (*b*) raised the viscosity only from 3·73 to 3·83. According to the supplier, (*e*) was prepared by precipitation with aluminium salts and extraction with a solution of hydrochloric acid in alcohol; addition of 20 per cent. of aluminium nitrate to the solution of (*b*), however, changed the viscosity to 3·48, and produced a flocculent precipitate. Five g. of (*a*) were digested overnight with 100 ml. of 80 per cent. alcohol and 2 ml. of hydrochloric acid in the cold, and the residue was then removed from the extract (mainly calcium salts) by filtration and washed with the 80 per cent. alcohol until neutral, and then with absolute alcohol followed by dry ether; the ash-content fell to 3·35 per cent., and the 0·75 per cent. solution was less cloudy than originally and similar to that of (*e*), and had a viscosity of 6·62. The high viscosity of (*e*), therefore, appears to be due to the fact that the ash has been reduced by extraction with acid (*cf.* Baker and others, *Ind. Eng. Chem.*, 1926, **17**, 89; *Delaware Agr. Exp. Stat. Bull.*, 1927, **149**; 1934, **187**; and following abstract). J. G.

Pectin in Hops. H. Fink and J. Hartmann. (*Woch. Brau.*, 1935, **52**, 221; *J. Inst. Brewing*, 1935, **41**, 380.)—Although the presence of pectin in hops has not hitherto been reported, it occurs in almost all non-woody vegetable tissues (*e.g.* roots, fruits and plant stems). It would remain undissolved by the solvents used to extract the bitter substances of hops, and might be overlooked in the extraction of hop tannins. For the detection of pectin (after F. Ehrlich) the material is digested with 10 to 15 times its weight of 1 per cent. sulphuric acid at a

pressure of 4 atm. in order to produce galacturonic acid by hydrolysis, and this may be detected by known reactions. Pectins may then be determined by extracting the minced hops with alcohol and ether, 10 g. of the air-dry residue being boiled with 1 litre of 0·01 *N* citric acid under a reflux condenser for 24 hours. The liquid obtained after filtration is concentrated under reduced pressure to 250 ml., the calcium pectate in 40 ml. of this concentrate being determined by Mehlitz's method (*cf.* preceding abstract). Positive results with Ehrlich's test were obtained for hops, but not for ground barleys and malts, and 2 per cent. of pectin (calculated on the dry weight of the hops after extraction with alcohol and ether) was found by the quantitative method. It is considered that this quantity may be important from the brewing standpoint. J. G.

Constituents of the Wax-like Coating of the Pear, *Pyrus communis* L. K. S. Markley, S. B. Hendricks and C. E. Sando. (*J. Biol. Chem.*, 1935, **111**, 133–146.)—Peels obtained in the commercial canning of pears were extracted with ether and also with petroleum spirit. The ethereal extract, after further extraction with petroleum spirit, yielded ursolic acid. The extract obtained by petroleum spirit extraction contained about 40 per cent. of free and combined acids, approximately one-third of which were in the unesterified state. The solid acids, which comprised about one-eighth of the total acids, consisted of the usual mixed plant acids of the series C_{16} to C_{24}. The predominant acid was oleic, and only very small quantities of linolenic and linolic acids were isolated. No secondary alcohols or ketones were detected, but a small amount of glycerol was present, as well as the usual plant alcohols, which were at least ternary mixtures of the series C_{20} to C_{30}. The predominant hydrocarbon was *n*-nonacosane $C_{29}H_{60}$. The light green, low-melting pear wax, which was described by Seifert (*Landw. Versuchs.-Stat.*, 1895, **45**, 29), was, therefore, a complex mixture of free acids, esters, alcohols, and hydrocarbons, and his uncrystallisable *vitin-like* substance, which melted at 240° C., was impure ursolic acid. S. G. S.

Daturic Acid from the Seeds of *Datura stramonium*, Linn. B. L. Manjunath and S. Siddappa. (*J. Indian Chem. Soc.*, 1935, **12**, 400–404.)—Daturic acid, which has been regarded as equivalent to margaric acid, is the only acid with an uneven number of carbon atoms, the presence of which has hitherto been regarded as proved in an oil, but its presence in the oil from *Datura stramonium* seeds is not confirmed by the present work. The methyl esters of the solid fatty acids of the oil were repeatedly fractionated by the method of Francis, Piper and Malkin (*Proc. Roy. Soc.*, 1930, [A], **123**, 214), but no trace of daturic acid could be found. Palmitic, stearic and a small quantity of lignoceric acids only were present. A phytosterol of m.p. 134° C. was isolated from the unsaponifiable matter.
D. G. H.

Thiocyanogen Value of Indian Butter Fat (Ghee). U. D. Budhalakoti and K. C. Mukherji. (*J. Indian Chem. Soc.*, 1935, **12**, 455–458.)—Ten authenticated samples of butter or butter-fat from various parts of India were examined to find whether their linolic acid content, as estimated by determination of the thiocyanogen and iodine values, was sufficiently constant to be an index

of purity. The percentage of linolic acid was found by multiplying the difference between the iodine value and thiocyanogen value by 1·104. The range of iodine values was wide (30 to 50), but that of the linolic acid content varied only from 3·5 to 5·4, so that this method appears equally applicable to Indian and Irish butters (*cf.* Arup, ANALYST, 1932, **57**, 610). D. G. H.

Detection and Determination of 2:4-Dinitrophenol in Tablets and Capsules. I. S. Shupe. (*J.A.O.A.C.*, 1935, **18**, 464–466.)—In the examination of these materials, which are used in the treatment of obesity, grinding and heating should be avoided, since otherwise explosion may occur. To detect 2:4-dinitrophenol, a sample is treated with water and 4 per cent. of sodium hydroxide, and the liquid filtered, if necessary. The filtrate is acidified with hydrochloric acid and extracted with chloroform. The extract is evaporated to small bulk on a water-bath, the last portions of the solvent being allowed to evaporate spontaneously. Part of the residue is treated with 2 ml. of 10 per cent. sulphuric acid and about 0·2 g. of powdered zinc and left for 10 minutes; appearance of a pink colour indicates nitrophenol. The liquid is then filtered, cooled, treated with 10 drops of 1 per cent. sodium nitrite solution, and, after remaining in the dark for 5 minutes, with 2 ml. of a saturated solution of β-naphthol in strong ammonia. After being left for 2 minutes, it is shaken with 10 ml. of ether, which assumes a pink or violet colour. From another portion of the residue from the chloroform extract, a 1 per cent. solution in 0·1 *N* sodium hydroxide is prepared and a drop of this treated, on a microscope slide, with a drop of 1 per cent. hydrochloric acid; microscopic examination shows characteristic rectangular, pale yellow crystals. The m.p. (114° C.) of the chloroform residue, recrystallised if necessary, and also the mixed m.p. with authentic 2 : 4-dinitrophenol, should also be determined.

To determine the dinitrophenol, a weighed quantity of the capsules (at least 20) is macerated with 20 ml. of 2 per cent. sodium hydroxide solution, which is transferred, with the aid of a little water, to a separating funnel, acidified with concentrated hydrochloric acid, and extracted with six successive portions of chloroform. The combined extracts are shaken with 20 ml. of 4 per cent. sodium hydroxide solution, and the lower layer is removed and repeatedly extracted with 20 ml. portions of the alkali until the yellow colour is eliminated. The alkaline solutions are mixed and made up to volume with water in a measuring flask. An aliquot part, containing about 0·1 g. of the dinitrophenol, is transferred to a glass-stoppered flask, diluted with water to 100 ml., neutralised with hydrochloric acid, and then made slightly alkaline with 4 per cent. sodium hydroxide solution. Twenty ml. of 0·1 *N* bromine solution are pipetted in, and 5 ml. of concentrated hydrochloric acid are added, and the stopper is at once inserted. The flask is shaken for a minute and cooled, 10 ml. of 15 per cent. potassium iodide are added, and the stoppered flask is thoroughly shaken. The stopper and neck of the flask are rinsed down, and the liquid is shaken with 1 ml. of chloroform, and titrated with 0·1 *N* sodium thiosulphate, with starch as indicator : 1 ml. of 0·1 *N* bromine $\equiv$ 0·0092 g. of dinitrophenol $\equiv$ 0·0103 g. of the anhydrous or 0·0112 g. of the monohydrated sodium derivative. T. H. P.

Determination of Hexamethylene-tetramine. R. Gros. (*J. Pharm. Chim.*, 1935, **127**, 241–244.)—Since hexamethylene-tetramine is hydrolysed by dilute sulphuric acid to formaldehyde and ammonia, the purity of a sample may be ascertained by determining the proportions of these products. To determine the formaldehyde, a 200-ml. refrigerating pipette connected with a 500 ml. Erlenmeyer flask is used (*cf.* Gros, *J. Pharm. Chim.*, 1934, **126**, 421). Eighteen ml. of Nessler's reagent (specially prepared a few hours before it is required by mixing 80 ml. of a solution of 13·55 g. of mercury chloride and 36 g. of potassium iodide in 250 ml. of water with 100 ml. of a solution containing 270 g. of sodium hydroxide per l. and filtering) and 2·5 ml. of a suspension of barium sulphate (10 per cent.) are introduced into the bulb of the apparatus, and, after a vacuum of 15 to 18 mm. of mercury has been obtained, 5 ml. of a 0·2 per cent. solution of hexamethylene-tetramine, about 10 ml. of distilled water, and 1 ml. of *N* sulphuric acid are added by means of the safety tap. After 10 minutes on the water-bath at 80° C., the refrigerator is brought into action, still with the mixture on the water-bath. Distillation is carried nearly to dryness, after which atmospheric pressure is restored in the apparatus, and without disconnection of the cold-water circulation, about 10 ml. of dilute hydrochloric acid (1 : 2) are introduced into the bulb (which is shaken), and then 20 ml. of a 0·05 *N* iodine solution are added. The water circulation is stopped, the rubber tubes are removed, and the bulb is separated from the flask, with shaking from time to time to assist solution of the reduced mercury. After 2 to 3 minutes the contents of the bulb are rinsed into a 500-ml. flask, and the excess of iodine left after complete solution of the mercury is titrated with a 0·05 *N* solution of sodium thiosulphate. The sample then contains $(20-n)\times 3\cdot 5/6$ mg. of hexamethylene-tetramine, where n is the number of ml. required in the titration.

To determine the proportion of ammonia formed, 20 ml. of 0·02 *N* sulphuric acid are put into the refrigerating pipette, and into the Erlenmeyer flask (the walls of which have been washed to bring down the ammonium sulphate previously formed) are introduced 2 drops of phenolphthalein solution. After the necessary adaptations to the apparatus have been made and the vacuum established, baryta water is slowly introduced by means of the safety-tube until the mixture is alkaline; heating and distillation are then carried out as before. The atmosphere of the apparatus is washed with 10 ml. and then six times with 5 ml. of water each time. Atmospheric pressure is restored, the flask is disconnected, and the distillate and the washings are boiled to expel carbon dioxide. After cooling, 2 drops of a 1 per cent. solution of neutral red are added, and the excess of sulphuric acid is titrated with a 0·02 *N* solution of sodium hydroxide. If n ml. are needed, the proportion of hexamethylene-tetramine in the sample was $(20-n)\times 0\cdot 7$ mg. Various samples examined by this method gave results varying from 98 to 100 per cent. D. G. H.

Artificial Resins as Containers for Drugs. P. Pinten. (*Chem.-Ztg.*, 1935, **59**, 787.)—The odour of ammonia which is sometimes apparent when empty containers made from phenol plastics are opened (cf. *id.*, 1935, **59**, 636) is not due to decomposition, but to the production of ammonia from hexamethylene-tetramine during the manufacturing process. This gas appears to be retained by the surface

of the resin and is evolved only slowly; it is associated chiefly with the novolac resins and, to a far less extent, with the resoles, and it may be removed by heating the resin at 140° to 150° C., a process which also produces a harder product of greater chemical stability. In general, the phenol-content of the phenol resins decreases slowly in damp air, but this decrease is very small with properly hardened resins, and gives rise to trouble only in rare cases. Thus, hot coffee made by infusion in a resin container may acquire a phenolic taste, although cold coffee will not. Neutral substances, weak acids and fats in ointments, are without influence on such containers, but strong alkalis attack them. The choice of raw materials is important to ensure stability, and when *o*- or *p*-cresol is used for cheapness, resinification may be incomplete, and the material will become distinctly soluble. It is suggested that the harmful effect of the vapours of phenol or formaldehyde may be overrated, as workers exposed to them in high concentrations develop no serious symptoms. Great care is necessary, however, in handling the resin in the powdered form, not because of the evolution of phenolic vapours, but because it affects the lungs in a manner similar to siliceous dusts. Amino plastics (*e.g.* pollopas) are probably the least objectionable of these resins, and vessels made from the polystyrol (trolitul) type are unaffected by water, acids, alkalis or alcohol. Ampoules made from it are as hygienic as glass and much stronger.

J. G.

Biochemical

Deuterium as an Indicator in the Study of Intermediary Metabolism. I. R. Schoenheimer and D. Rittenberg. (*J. Biol. Chem.*, 1935, **111**, 163–168.)—I. The use of the hydrogen isotope, deuterium, is proposed for the study of intermediary metabolic processes. The concentration of deuterium can be determined in small samples with a high degree of accuracy, and therefore the fate of a physiological substance in which some of the hydrogen has been replaced by the deuterium can be traced in the organism after administration. Stearic acid, 6–7–9–10d_4, was prepared from linolic acid by shaking 4·5 g. of methyl linolate with about 100 mg. of platinum oxide in dry petroleum spirit at room temperature in an atmosphere of deuterium for 85 minutes. The ester was saponified, and the acid was liberated and recrystallised from alcohol. It contained 10·87 per cent. of deuterium (calculated 11·11 per cent.).

II. *Ibid.*, 169–174. The deuterium is produced by the electrolysis of a dilute solution of D_2SO_4 in D_2O in the cell, *a* (see Fig. 1). The gases are dried by passing them through the traps, *b* and *c*, immersed in solid carbon dioxide. The oxygen bubbles through the mercury to the air, while the deuterium bubbles up into the bulb *d*. The gas in *d* is periodically discharged into the 5-l. storage reservoir, *e*, in which the pressure is kept less than one atmosphere. With the aid of the Toepler pump, *f*, the gas may be transferred to the reaction bulb or pumped back from the reaction bulb to the storage reservoir. The trap, *g*, is immersed in solid carbon dioxide and prevents the vapours of the solvent in the hydrogenation vessel from diffusing back into the storage reservoir, *e*. The hydrogenation is carried out in ordinary hydrogenation bulbs. The amount of

gas absorbed during the hydrogenation may be calculated from the change of pressure in the system as shown by the manometer, *b*. The only rubber connection in the apparatus is between the trap, *g*, and the hydrogenation flask. Hydrogenation with deuterium must not be carried out with unsaturated substances, such as acids or alcohols, for the hydrogen would interchange with the deuterium gas in which the substance is shaken, and a part of this hydrogen would enter the double bond. In order to hydrogenate such substances, esters or other derivatives must be used. The method of determining the deuterium-content of any material is, in general, the same as that used for the determination of carbon and hydrogen

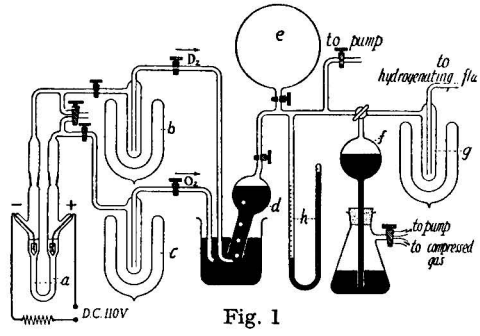


Fig. 1

in organic substances. The difference is that instead of the water formed being absorbed by a hygroscopic salt, it is frozen out by solid carbon dioxide. The oxygen passes over heated copper oxide, and is then dried by passage through a trap immersed in solid carbon dioxide. The dried oxygen is carried over the heated substance contained in the usual boat, and the water formed is frozen out in another trap, which is immersed in solid carbon dioxide. The amount of material used varied from 0·07 to 1·0 g., depending upon the probable deuterium-content. The water so obtained was then purified by the following procedure:—The trap containing the water was connected with another quartz combustion tube filled with copper oxide and heated to 750° C. A slow stream of dry oxygen carried the water vapour through the quartz tube, and the water was again frozen out in a similar trap. When all the water had been collected, a few crystals of chromic acid were added, and the trap was connected through an all-glass joint with a distillation system composed of three traps in series, the first of which contained 2 to 10 mg. of solid potassium hydroxide and a few crystals of potassium permanganate. The other two traps were empty, but the last one was connected with a two-way tap, so that a vacuum could be applied or air admitted. Air was admitted, the ice melted, and the water was gently boiled for 3 minutes. After cooling, the water was distilled *in vacuo* to the second trap. Air was again admitted, the ice melted, and the water was distilled *in vacuo* to the third trap. The concentration of deuterium was now determined. If the concentration of deuterium (in per cent.), multiplied by its weight in g., exceeded 0·2, the deuterium was determined by the difference in refractive index between H_2O and D_2O. This was done in a Zeiss interferometer, the difference being 0·00462 for the sodium D line at 20° C. If the amount of deuterium was less than this amount, it was estimated by determining the density of the water by means of a submerged-float

method. The purified water obtained by the method described above was diluted to 2·5 ml. with pure distilled water and distilled *in vacuo* into a small tube containing a glass float which was so constructed that it just floated in water at 0° C. and at atmospheric pressure. The receiver was maintained in a bath of ice and distilled water in a Dewar flask, and attached to the neck of the receiver was a series of stopcocks by means of which the pressure inside the receiver could be varied and measured on a manometer. If the pressure was lowered, the float rose, and the time was taken for it to pass two cross-hairs in the field of a microscope. If the pressure was increased, the float fell and similar readings were taken. By plotting the velocities obtained in this way against the pressures as read on a manometer, a straight line was obtained, and the floating pressure determined. In the apparatus used, a change in pressure equivalent to 1 cm. of mercury corresponded with a change in density of 0·376 p.p.m. Since the density of pure D_2O is 1·1079, a change of 1 p.p.m. in the density corresponds with about 0·001 per cent. of deuterium.

III. *Ibid.*, 175–181. Mice were fed from 2 to 10 days on a diet composed of 20 per cent., 4 per cent., and 1 per cent. of deuterium-containing fats. At the end of this period the deuterium-content of the fat depôts, the fat of the internal organs, and the body fluids was determined. Much of the diet fat was found in the fat depôts. In experiments with mice fed for 4 days on a diet containing 1 per cent. of fat, 47 per cent. of the ingested fat was found in the depôts, and heavy water equivalent to 20 per cent. of the ingested fat in the body fluids. A small amount of the absorbed fat was found in the internal organs. These experiments indicated that, even when it is present in small quantities, the largest part of the diet-fat was deposited in the fat tissues before it was utilised.

S. G. S.

Lead-content of Human Tissues and Excreta. S. L. Tompsett and A. B. Anderson. (*Biochem. J.*, 1935, **29**, 1857–1864.)—A method, which is claimed to be an accurate one, is described for the determination of lead in human tissues, blood and excreta. The material under investigation is ashed and the lead is extracted with ether as a complex with sodium diethyldithiocarbamate. The lead in the ethereal extract, after the destruction of the organic material, is determined colorimetrically with diphenylthiocarbazone. Lead was found in all the tissues examined, and the question whether this was present during life or was due to mobilisation of lead from deposits in the bones owing to metabolic changes preceding death is mentioned. The "normal" lead-content of the human body is also discussed. The recovery of lead added to serum already containing this metal varied from 90 to 120 per cent., and in a similar experiment with blood from 90 to 112 per cent. In the tissues examined the average values (in mg. Pb. per kg.) for adults were: liver 1·73, kidney 1·34, spleen 1·68, brain 0·5, rib 8·55, vertebra 7·09. Tissues from a case of known exposure to lead gave higher figures, especially for the rib, which was 119 mg. per kg. From the analysis of four foetuses of 7 to 8 months' gestation the following average amounts (in mg. per kg.) were obtained: liver 0·68, kidney 0·63, brain 0·7, and femur 1·73. Adult urine gave an average figure of 0·05 mg. per day, and

faeces 0·22 mg. for the same period. Blood from three normal persons and eighteen patients, none of whom was acutely ill, was also examined, and the values obtained varied from 40 to 70γ per 100 ml., with an average of 55γ. A solder-maker who exhibited symptoms of plumbism had blood with a varying lead-content, the maximum recorded being 380γ per 100 ml. S. G. S.

Precipitation of *l*-, *dl*-, and *m*-Cystine by Phospho-12-tungstic Acid. G. Toennies and M. Elliott. (*J. Biol. Chem.*, 1935, **111**, 61–74.)—If the precipitation of the phospho-12-tungstates of *l*-, *dl*, and *m*-cystine is carried out at 0° C., and the solutions left at that temperature for several days, the reaction proceeds until nearly complete. The precipitates should be filtered off on an ice-cooled Buchner funnel and sucked dry before analysis. In the presence of *N* hydrochloric acid solution, *m*-cystine can be precipitated to a residual concentration of $5 \times 10^{-4}M$ in the presence of $2 \times 10^{-2}M$ phosphotungstic acid. The corresponding concentrations for *dl*-cystine are $1{\cdot}5 \times 10^{-5}M$ and $4 \times 10^{-2}M$, whilst for *l*-cystine these become $1 \times 10^{-5}M$ and $1 \times 10^{-2}M$. Previous statements concerning the constitution of cystine phosphotungstates were not confirmed, for in a constant medium (*N* hydrochloric acid solution) the crystalline precipitates vary in their composition according to the ratio of cystine to phosphotungstic acid used. The precipitates were examined for sulphur by a modification of the Blix potassium permanganate method, after removal of the phosphotungstic acid by amyl alcohol, and the phosphotungstic acid was determined by ignition. *l*-Cystine was also determined by the optical rotation of the phosphotungstate in acetone solution. In *N* hydrochloric acid solution, containing 31 to 32 per cent. by volume of acetone, within a concentration range of 2·5 to 4·8 g. of cystine per 100 ml., in the presence of 27 to 60 g. of phosphotungstic acid, the value for $[\alpha]_g^{25}$ was $-236° \pm 2°$ with a temperature coefficient of $-2{\cdot}2°$. S. G. S.

Leaf Carotenes. G. MacKinney. (*J. Biol. Chem.*, 1935, **111**, 75–84.)—Carotenes derived from the leaves of 59 different plant species, distributed in forty botanical families were examined, and it was found that in all cases the major fraction was β-carotene. In the material from forty of these sources α-carotene was found in amounts varying from a trace up to 35 per cent. of the total carotene present. By the use of an adsorbent the presence, in traces, of another carotenoid was detected. The application of phylogenetic considerations to the prediction that leaves of closely-related plants or groups of plants would give carotene complexes which did not differ materially from one another, was fairly successful; but at present there is no adequate explanation of the presence or absence of α-carotene in any specific plant. S. G. S.

Carotenes from Different Sources and Some Properties of α- and β-Carotene. H. S. Strain. (*J. Biol. Chem.*, 1935, **111**, 85–93.)—Carotenes from a number of natural products were isolated and separated by the use of adsorption columns composed of magnesium oxide. In every instance β-carotene was the principal component of the mixtures, which often contained α-carotene, as well as other carotenoids, more strongly adsorbed than β-carotene. Material from the petals of the Californian poppy, the leaves of the white carrot,

and butter contained a carotene which was less readily adsorbed than α-carotene, and which appeared to be identical with a similar carotene previously isolated from palm oil. Most sources of carotene contained colourless substances which influenced the adsorption of carotene and which often crystallised with it, even after it had been isolated by adsorption. Chlorinated solvents were then used, instead of petroleum spirit and *n*-heptane, for recrystallisation. The optical rotation of α-carotene was, in dichloroethylene $[\alpha]^{18}_{667\cdot8} = +338° \pm 10°$, in benzene $[\alpha]^{19}_{667\cdot8} = +344° \pm 10°$, in pyridine $[\alpha]^{18}_{667\cdot8} = +362° \pm 10°$, in carbon disulphide $[\alpha]^{17}_{667\cdot8} = +392° \pm 10°$; β-carotene was inactive. The difference between the two wave-lengths at maximum absorption was constant at about $30m\mu$ for both isomers, and the difference between the corresponding maxima for α- and β-carotene was also constant at about $6m\mu$. The specific gravities of the isomers were identical; 1·000 ± 0·004 referred to water at 20° C. Both gave characteristic colours with antimony trichloride solution in chloroform and also with trichloroacetic acid in the same solvent. Dichloromethane and 1, 2-dichloroethane were also used for these colour tests. S. G. S.

Water

Colour-scale for the Rapid Determination of Nitrates in Water. R. Gros. (*J. Pharm. Chim.*, 1935, **127**, 244–246.)—The official colorimetric method of the Laboratoire du Conseil Supérieur d'Hygiene for the rapid determination of nitrates in water consists in evaporating in two glass capsules 10 ml. of the water under examination and 10 ml. of a solution of 0·081 g. of pure melted potassium nitrate in 1 l. of water (10 ml. are equivalent to 0·5 mg. of nitric acid), respectively, and adding to each of the cooled residues 1 ml. of a solution of 3 g. of crystallised phenol in 37 g. of sulphuric acid (sp.gr. 1·84). Five ml. of water, followed by 10 ml. of dilute (1 in 3) ammonium hydroxide, are then added, a yellow colour, due to the ammonium salt, resulting. The control corresponds with a content of 50 mg. of nitric acid per l. Colours are compared in a Duboscq colorimeter after interposition of a blue glass. A scale of stable colours may be used to eliminate the use of the colorimeter, and for this purpose a solution is used which contains in 100 ml. (*a*) dried recrystallised potassium dichromate 0·1 g.; (*b*) nickel sulphate ($NiSO_4.7H_2O$), 2 g.; (*c*) 10 drops of concentrated sulphuric acid. The scale corresponds with 10 to 50 mg. of nitric acid, when the following solutions are used:—for 10 mg. of nitric acid, 2 ml. of $a + b$, 14 ml. of *c*; for 20 mg., 40 ml. of $a + b$, 12 ml. of *c*; for 30 mg., 6 ml. of $a + b$, 10 ml. of *c* for 40 mg., 8 ml. of $a + b$ and 8 ml. of *c*, and for 50 mg. 10 ml. of $a + b$, 6 ml. of *c*. By interpolation, nitrates in water may be estimated within 5 mg. per l.

D. G. H.

Agricultural

Selenium in Soils in Relation to its Presence in Vegetation. H. G. Byers and H. G. Knight. (*Ind. Eng. Chem.*, 1935, **27**, 902–904.)—Selenium occurs in soils to a varying extent, and in certain localised areas it is present in quantities sufficient to render vegetation toxic. So far, the soils found to contain serious

quantities of selenium are heavy clays which have developed from shale deposits of the Cretaceous period. The primary source of the selenium appeared to be iron pyrites or other sulphide minerals containing selenium. No sandy soils contained more than a trace of selenium. Various factors connected with entry of selenium into plants have been examined. The capacity of different plants to absorb selenium varied considerably. Thus with a one square-mile plot of land in S. Dakota the following results were obtained for the selenium-content of soil and vegetation:

Material	No. of samples	Selenium (p.p.m.) range	mean
Soil (surface)	122	0·7–13	4·8
Wild aster	1	—	2670
Western wheat grass ..	12	—	20
Little bluestem ..	50	—	0·8
All vegetation	137	—	36

It was also found, for example, on experimental plots in Wyoming, that, whereas the soil contained about 2 p.p.m. of selenium, vegetation contained selenium as follows (p.p.m.): Mixed grasses, 10; *Astragulus missouriensis*, 3; *A. bisulcatus*, 1250. Some plants, therefore, are highly absorptive of selenium. These results were obtained with plants grown under relatively dry conditions, and there are indications that, on well-watered soils, contamination of plants by selenium is minimised by reason of the selenium being washed out of the surface layers of the soil. Thus, irrigation in dry areas might be a remedy for the selenium trouble, and this point is to be further studied. The distribution of selenium in the plants is irregular, and, in general, more selenium is found in the leaf than in the stem or seed. Thus, wheat leaves in a given sample contained 40 p.p.m. of selenium, whilst the stalks and grain contained 12 p.p.m. and 8 p.p.m., respectively. In seleniferous wheat the selenium is largely concentrated in the wheat gluten. S. G. C.

Determination of Base-Exchange in Soils by means of Copper. J. Lavollay. (*Ann. Chim. anal.*, 1935, **17**, 229–230.)—Fieger, Gray and Reed (*Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 281) treated the soil with copper nitrate solution. The amount of copper rendered insoluble by the soil was found indirectly by determination of the diminution in strength of the copper solution. It is now pointed out that this procedure does not give a true value of the base exchange of soils containing calcium carbonate, because some copper is thereby precipitated as basic copper carbonate. It is therefore preferable to determine directly the copper precipitated as a result of base exchange, as in the following method, which involves acting on the soil, after copper nitrate treatment, with sodium acetate solution; the basic copper carbonate remains undissolved, whilst the copper absorbed in the soil becomes replaced by sodium and re-dissolves, and may be determined in the sodium acetate extract by precipitation with 8-hydroxyquinoline. *Method.*—To 25 g. of the fine soil are added 200 ml. of copper nitrate solution (10 per cent.), and the mixture is kept for 24 hours, with occasional shaking. The soil is filtered off on a Buchner funnel and washed with alcohol. About 200 ml. of sodium acetate solution (14 per cent.) are poured slowly over the soil on the funnel. An aliquot part of the filtrate containing the extracted copper is acidified

with acetic acid and boiled to remove alcohol. The *p*H value is adjusted to about 5·4 (reddish colour with methyl orange), and the copper is precipitated from the hot solution by 8-hydroxyquinoline. The precipitate is filtered off, washed with hot water, dried at 105° C. and weighed as $(C_9H_6ON)_2Cu$. S. G. C.

Organic

Determination of Methyl Alcohol in Alcoholic Products. J. B. Wilson. (*J.A.O.A.C.*, 1935, **18**, 477–488.)—The various methods which have been proposed for the determination of methyl alcohol in presence of ethyl alcohol are discussed. Those depending on oxidation of the methyl alcohol to formaldehyde are regarded as of doubtful value, owing to the uncertainty of the oxidation being complete. Flanzy's method (Abst., ANALYST, **1935**, 632) is tedious, as it involves several operations, including two determinations, and a small error in either of these would considerably affect the results. In the method now described, as in that of Flanzy, the methyl and ethyl alcohols are converted into the corresponding iodides, which are partially separated by fractionation and are then converted respectively into tetramethylammonium iodide and trimethylethylammonium iodide by the action of trimethylamine. The first of these quaternary iodides is then separated by precipitation from absolute alcohol, in which it is only very sparingly soluble, and is weighed in a sintered glass crucible. The details of the procedure to be followed are described. Sugars and other substances which use up iodine interfere, but may be eliminated by distillation. Methyl esters and ethers and other compounds containing a methoxy group form methyl iodide and should be removed beforehand. Vanillin and other non-volatile constituents are removable by distilling the alcohols. Methyl esters and ethers are volatile and may be expelled by the procedure recommended by Thorpe and Holmes; a modification of this is now described. Results obtained by applying the method to samples of known composition and to various alcoholic beverages are given. T. H. P.

Use of Kaolin in the Method for Determining Non-tannins. A. Jamet. (*J. Int. Soc. Leather Trades Chem.*, 1935, **19**, 394–395.)—Baldracco's recent statement, to the effect that the use of kaolin in the determination of non-tannins introduces error, owing to adsorption of vegetable non-tannins by the kaolin, is examined. It is found that the non-tannins obtained by the Baldracco-Darmstadt method contain soluble protein substances, owing to inadequate washing of the dry hide powder. When the official method is used, in conjunction with the Jamet and Darmstadt apparatus and without kaolin, the non-tannins obtained are free from all traces of protein. T. H. P.

Volumetric Determination of Camphor by the Hydroxylamine Method. R. Vandoni and G. Desseigne. (*Bull. Soc. Chim.*, 1935, **2**, 1685–1691.)—In the modification proposed by the authors, 50 ml. of 2 *N* hydroxylamine hydrochloride are introduced into a 100-ml. flask having a ground-in reflux condenser. After addition of 0·2 ml. of the indicator the solution is brought to the same colour as a standard prepared by dissolving 7 g. of hydroxylamine hydrochloride in 25 ml. of water and 40 ml. of 95 per cent. alcohol, adding 0·2 ml. of a 1 per cent. alcoholic

solution of bromphenol blue, and bringing the mixture to the neutral point (green) by adding 0·3 ml. of *N* sodium hydroxide solution. One g. of sodium carbonate (accurately weighed) is added, and 1 to 2 g. of the substance to be analysed. The mixture is boiled gently for about 1 hour under the reflux condenser on a water-bath, and then allowed to cool to about 30° C. At the end of the reaction the solution should still be alkaline to bromphenol blue. *N* hydrochloric acid is then run in from a burette until the solution is distinctly yellow, and, when the sodium carbonate is entirely dissolved, the liquid is titrated back to the standard colour with *N* sodium hydroxide solution. Since hydroxylamine hydrochloride is slowly decomposed when boiled in dilute alcoholic solution with sodium carbonate a correction factor must be applied, 0·0003 mol. being deducted from the number of mols. found by titration. The method also gave satisfactory results with carvone, menthone and camphylene, but with fenchone the results were about 6 per cent. too low. The procedure may also be applied to the determination of camphor in organic liquids not miscible with water. A little absolute alcohol may be added at the time of titration to obtain a homogeneous solution, though the end-point can be observed in a heterogeneous mixture. Finally, the method may be used for the determination of camphor in nitrocelluloses after saponification, the aqueous solution being extracted with a suitable solvent. A. O. J.

Inorganic

Use of 8-Hydroxyquinoline in the Determination of Aluminium, Beryllium and Magnesium. H. B. Knowles. (*Bur. of Standards J. Research*, 1935, **15**, 87–96.)—Aluminium can be quantitatively precipitated and separated from beryllium and magnesium at *p*H 6·8. *Method* (*a*). *In absence of beryllium.*—To the solution (200 ml.), containing about 10 ml. of hydrochloric acid, tartaric acid is added in amount equal to 5 times the weight of aluminium present.* Fifteen ml. of ammonium acetate solution (30 g. of ammonium acetate dissolved in 75 ml. of water) and 8 to 10 drops of bromocresol purple indicator (0·04 per cent.) are added, followed by dilute ammonia until the indicator changes to purple. The solution is stirred, and a solution of 8-hydroxyquinoline in dilute acetic acid (12·5 g. of 8-hydroxyquinoline dissolved in 25 ml. of hot glacial acetic acid and diluted to 500 ml. and filtered) is added slowly in 15 to 25 per cent. excess. The liquid is heated to boiling, with occasional stirring, and boiled for 1 minute. After being allowed to cool to 60° C., the precipitate is filtered off on a sintered glass crucible of fine porosity (*e.g.* 1bG4), and washed with 100 ml. of cool water. The determination may be finished gravimetrically by drying the precipitate for 3 hours at 135° C., and weighing as $Al(C_9H_6ON)_3$, which contains 5·87 per cent. of aluminium or 11·10 per cent. of aluminium oxide. For volumetric determination, the crucible and contents are heated in a beaker containing 200 ml. of dilute hydrochloric acid (1 + 4) until the precipitate has dissolved; the crucible is removed, washed with dilute (1 + 9) hydrochloric acid, and the washings are added to the main solution, which is diluted to 400 ml. and cooled. Standardised potassium bromate-bromide solution (0·1 *N* solution should be used for amounts of aluminium up

* Abstractor's Note.—No statement is made that the amount of tartaric acid is critical.

to 10 mg., and N solution for amounts such as 50–100 mg.; N solution contains 27·835 g. of potassium bromate and 100 g. of potassium bromide per l.) is added in moderate excess (2 to 3 ml.) as determined by test after allowing 1 minute for complete bromination of the hydroxyquinoline (1 drop is withdrawn and added to a drop of potassium iodide and starch solution on a spot plate, a blue colour indicating an excess); 15 ml. of 20 per cent. potassium iodide solution are added, and the liberated iodine is titrated with standard sodium thiosulphate solution, starch being used as indicator; 1 ml. of N bromate-bromide solution ≡ 0·0022475 g. of aluminium. It was found in test experiments that accurate results (within a few tenths of a mg.) were obtained only when the amount of aluminium taken was not more than 25 to 50 mg.; with larger amounts there was a distinct positive error due to retention of the reagent in the precipitate; the error was more marked in the volumetric than in the gravimetric method. For accurate results with amounts of aluminium exceeding 50 mg., the following procedure is recommended: The oxyquinolate precipitate is dissolved in dilute sulphuric acid, the solution is evaporated "to fumes," and the organic matter is destroyed by the addition of nitric and perchloric acids; the aluminium is subsequently determined by precipitation as hydroxide in the usual way.

Method (*b*). *In presence of beryllium.*—The method is the same, except that tartaric acid is omitted. The beryllium may be determined in the filtrate by precipitation with ammonia in the usual manner; the excess of hydroxyquinoline present does not interfere with the precipitation of the beryllium provided the solution is allowed to cool before filtration. Test experiments showed that with up to 0·1 g. of aluminium and beryllium present the aluminium precipitate contained a maximum of 0·1 mg. of beryllium. The results for aluminium were not so good as were obtained by Method (*a*) (when tartaric acid was present), owing to somewhat greater co-precipitation of reagent.* *Separation from magnesium.*—The aluminium oxyquinolate precipitated in the presence of up to 0·1 g. of magnesium in solution by either Method (*a*) or (*b*) was found to retain less than 0·2 mg. of magnesium. *Determination of aluminium in felspar.*—Iron, titanium and other interfering elements are in general present in such small quantities as to make their prior removal unnecessary in ordinary work, and rapid routine determinations of alumina can be made by precipitating the aluminium from a solution obtained from 0·1 g. of feldspar after removal of silica. *Interfering elements.*—Numerous elements interfere in the above processes, such as the heavy metals, manganese, alkaline earth metals, iron, titanium and zirconium.

S. G. C.

Hexammine Cobaltic Compounds of Vanadium. W. G. Parks and H. J. Prebluda. (*J. Amer. Chem. Soc.*, 1935, **57**, 1676–1678.)—Parks ("Dissertation," Columbia University, 1930) found that the hexammine cobaltic ion reacted with quinquevalent vanadium solutions to yield the following: (*a*) in neutral solution: an apricot-coloured precipitate of hexammine cobaltimetavanadate:

* Abstractor's Note.—It is to be presumed that Method (*a*) would be satisfactory for separating aluminium from beryllium if determination of beryllium in the filtrate were not required.

(*b*) in alkaline solution: an orange-coloured precipitate of hexammine cobaltipyrovanadate; (*c*) in a solution buffered with acetic acid and ammonium acetate at *p*H 5·1: a yellow precipitate of hexammine cobaltideuterohexavanadate. These findings have been verified in the present investigation. Parks also found that in the acid medium, the vanadium was precipitated quantitatively and could thus be separated quantitatively from phosphate, arsenate, and ferric, cupric and calcium ions, but not from tungstate, molybdate or lead ions. No tests of these further statements were carried out by the present authors. S. G. C.

Detection and Determination of Gold by means of Carbon Monoxide. R. N. Costeanu.—(*Z. anal. Chem.*, 1935, **102**, 336–338.)—Solutions of gold chloride are reduced to colloidal gold by carbon monoxide; a filter paper soaked in a gold solution turns purple in a stream of the gas. The colour increases in intensity with the gold concentration. For a colorimetric determination of gold in an alloy, the filings (0·025 g.) are first extracted with nitric acid; the insoluble residue is dissolved in *aqua regia*, the liquid is evaporated, and the chloride is dissolved in 25 ml. of water. Strips of filter-paper are moistened with the solution, allowed to drain, and placed in a horizontal glass tube. In a parallel tube are placed strips of paper impregnated with gold solutions of known concentration (*e.g.* 1, 0·5, 0·25, etc., mg. Au per ml.). The tubes are connected with a generator containing formic and sulphuric acids; the carbon monoxide is dried over phosphorus pentoxide before passing over the test-papers. W. R. S.

Determination of Chromium in Chrome-tanned Leather. G. F. Smith and V. R. Sullivan. (*J. Amer. Leather Chem. Assoc.*, 1935, **30**, 442–453.)—The method involves destruction of the leather and oxidation of the chromium by wet oxidation with perchloric acid, and titration of the chromic acid formed. The digestion process may be accelerated by means of catalysts such as vanadic acid or osmic acid. *Method.*—To a 1-g. sample of the leather contained in a 500-ml. conical flask are added 15 ml. of oxidising solution (2 vols. of 70 per cent. perchloric acid and 1 vol. of sulphuric acid, sp.gr. 1·73) and 5 ml. of concentrated nitric acid. The mouth of the flask is closed by a thistle funnel having a sealed off stem bent so as to touch the inside surface of the flask. The liquid is digested at a temperature between 175° and 200° C., at which it boils quietly. When oxidation is complete, the solution is cooled somewhat by dipping the flask (after giving it a rotatory motion) in cold water for 4–5 sec., diluted with 30 to 40 ml. of water, and boiled 2 to 3 minutes to remove chlorine. The solution is further diluted to 200 ml., cooled, 1 ml. of 85 per cent. phosphoric acid and a few drops of sodium diphenylamine sulphonate indicator solution (0·005 *M*) are added, and the chromic acid is titrated with 0·05 *N* ferrous sulphate solution until the initial purplish colour changes to light green. *Use of catalyst.* (*a*) *Osmic acid.*—The procedure is the same as that above, except that approximately 0·2 ml. of 0·01 *M* osmic acid solution is added with the mixed acids at the start of the digestion process. (*b*) *Vanadium.*—About 30 mg. of ammonium vanadate are added in the digestion process. The following modified procedure for titration is required:—instead of the diphenylamine sulphonate indicator, 2 drops of *o*-phenanthroline ferrous sulphate solution (0·025 *M*) are added, followed by

a slight excess of 0·05 *N* ferrous sulphate solution (indicator colour changes to intense pink); 20 to 25 g. of sodium acetate trihydrate are added, the solution is heated to 50° C. and titrated with either 0·05 *N* ceric sulphate solution or 0·05 *N* potassium permanganate solution (grey to light bluish-green colour at end-point). Test experiments showed that an accuracy of ±0·02 per cent. may be expected. Vanadic acid is a somewhat more efficient catalyst than osmic acid. Various leathers required 18 to 41 minutes for destruction of organic matter without the use of catalyst, 17 minutes with osmic acid catalyst, and 11 to 16 minutes with vanadium catalyst; the leathers containing paraffin filling-materials required the longer time. S. G. C.

Determination of Vanadium in Uranium Salts. N. I. Tscherwjakow and E. A. Ostroumow. (*Z. anal. Chem.*, 1935, **102**, 181–186.)—The principle of the method consists in the oxidation of dimethyl-*p*-phenylenediamine by quinquevalent vanadium. The uranyl salt (sulphate or chloride; 0·2 to 0·5 g.) is dissolved in a minimum of water in a Nessler tube. Uranyl nitrate or acetate must first be converted into chloride. The tube serving for the colour standard contains an equivalent amount of pure uranium solution. The two solutions are treated with 5 to 6 drops of hydrochloric acid (1 : 1), 0·5 ml. of phosphoric acid, and at least four times the total volume of the liquid in alcohol; the total volume before this addition should not exceed 10 ml. Glycerin (3 to 4 ml.) is added, and the solutions are well stirred. The above procedure converts any ferric salt present into a stable complex glycerin ester. If the solution becomes cloudy at this point, it is cautiously treated with dilute hydrochloric acid until clear; the standard should be treated exactly like the assay. One ml. of a 0·5 per cent. solution of the base (sulphate or hydrochloride) is added to each tube, and they are shaken for half a minute. The red tinge of the unknown solution is then matched by titration of the standard with a vanadate solution of known strength. Four minutes are allowed to elapse before the final adjustment is made. The method may be applicable to the determination of minute amounts of vanadium in other preparations. If the iron-content is high, previous fusion with sodium carbonate is necessary. W. R. S.

Volumetric Determination of Iodide with an Iodine-Starch Indicator. E. Chirnoaga. (*Z. anal. Chem.*, 1935, **102**, 339–342.)—The method of Kolthoff (*Pharm. Weekbl.*, 1917, **54**, 761) consists in the addition of a little iodate (or iodine) and starch solutions to the slightly acidified iodide solution, and titration with silver nitrate. The author avoids introducing an iodine compound by the following modification. The neutral or acid (10 ml. of 0·1 *M*) solution is treated with 2 drops of saturated ferric sulphate solution and 2 ml. of 0·4 per cent. starch solution, and titrated with 0·1 *N* silver nitrate solution. The colour changes from blue to green, the precipitate adsorbing the blue starch compound. The precipitate appears orange immediately before, and characteristically yellow at, the end-point. In presence of chloride, 10 ml. of 2 *M* sodium acetate solution must be added with the ferric sulphate and starch solutions. The procedure permits of the determination of the chloride also; the silver iodide is filtered off and washed three times with water. The filtrate is treated with 2 to 3 ml. of

ferrous ferricyanide indicator (Abstr., ANALYST, 1935, 428), and titrated with silver nitrate solution until the precipitate is colourless. If bromide also is present, the titration must be carried out in ammonium carbonate solution, as prescribed by Kolthoff. W. R. S.

Determination of Fluorine in Phosphorites by a Simplified Method. S. N. Rosanow. (*Z. anal. Chem.*, 1935, **102**, 328–336.)—The apparatus and technique applied in Penfield's evolution method have been simplified, with the result that a determination can be carried out in about four hours. The original paper gives constructional and manipulative details. W. R. S.

New Method for the Separation of Selenium from Sulphur. E. Cheraskowa and L. Weissbruth. (*Z. anal. Chem.*, 1935, **102**, 353. Preliminary communication.)—The method is based upon the differential stability between thiosulphate and selenothiosulphate, the latter only being decomposed by formaldehyde, with precipitation of selenium. The weighed substance, containing the two elements as such, is boiled under reflux with 100 ml. of 10 per cent. sodium sulphite solution for two hours. The cold extract is filtered, and the filtrate is treated with 50 ml. of formalin added through the reflux condenser. The selenium is precipitated on heating. It is collected after standing overnight, washed with cold water, hydrochloric acid (1 : 1) for the removal of any ferric oxide, then with hot water, and finally with alcohol and ether. The dried precipitate is weighed. The filtrate from the selenium is treated with 20 ml. of 20 per cent. acetic acid, and the thiosulphate is titrated with 0·1 *N* iodine solution. W. R. S.

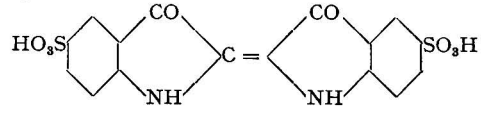
Gravimetric Determination of Selenate. R. Ripan-Tilici. (*Z. anal. Chem.*, 1935, **102**, 343–344.)—Lead selenate is more advantageous for gravimetric purposes than the barium salt, being more insoluble and crystalline. The boiling selenate solution (about 0·01 *M*) is treated, drop by drop, with a 0·5 *M* lead nitrate solution (0·1 to 0·2 ml. excess). The solution is kept boiling for a few seconds, and treated with enough alcohol to provide 30 to 35 per cent. in the liquid. The covered beaker is kept 4 to 5 hours at room temperature with occasional stirring. The precipitate is collected in a porous porcelain crucible and washed, by decantation first, with 30 per cent. alcohol. It is finally washed with strong alcohol, then ether, kept *in vacuo* for a short time, and weighed. A large excess of precipitant must be avoided, as lead selenate has a strong adsorptive power. W. R. S.

Microchemical

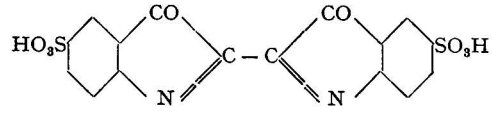
Chemical Microscopy of Gold and the Platinum Group. W. F. Whitmore and H. Schneider. (*Mikrochem.*, 1935, **17**, 279–319.)—The crystalline reactions of the elements were studied, by the usual methods of chemical microscopy. The elements tested were used in solutions of 1, 2 and 5 per cent. concentrations, and the reagents at 10 per cent. concentration, except the alkaloids, which were used in 1 per cent. solutions; when crystals did not form readily, as frequently happened, the reagent was used in the solid form. A large number of reactions are given

with illustrations of some of the crystals formed. The most characteristic reactions for each metal take place with the following reagents:—*Ruthenium*: (1) Tetraethyl-ammonium bromide, (2) methylamine hydrochloride. *Rhodium*, no satisfactory reagent. *Palladium*: (1) Dimethylglyoxime, (2) caffeine: *Osmium* must be separated by distillation, when crystals may be formed with potassium hydroxide. *Iridium*: (1) Methylamine hydrochloride. *Platinum*: (1) Meta-toluidine hydrochloride, (2) meta-phenylenediamine, (3) diethylamine hydrochloride. *Gold*: Caffeine. A method for the microscopic analysis of the group has been developed: in this method it is advisable first to separate gold from the rest of the group by extraction with ethyl acetate, and then osmium by distillation; the other metals (with the exception of rhodium) are then detected by testing with the reagents listed above. J. W. M.

Use of Indigo Carmine in Micro-volumetric Analysis. I. M. Korenman (*Mikrochem.*, 1935, **18**, 31–38.)—By oxidation under suitable conditions, indigo carmine (I), which forms a blue solution, gives the yellow compound disulphodehydro indigo (II).



(I)



(II)

To prepare a 0·01 *N* solution, 2·3311 g. of the sodium salt of indigo carmine, or 2·1111 g. of the free acid, are dissolved in water and the solution is diluted to 1000 ml. This solution should be diluted freshly each day to 0·001 *N*, as the weaker solutions do not keep. For titrations in alkaline solutions, the indigo carmine is standardised against 0·01 *N* potassium ferricyanide, 2 ml. of ferricyanide and 1 ml. of concentrated sodium carbonate solution being used. The colour-change from yellow to green marks the end of the titration. For titrations in acid solutions, the indigo carmine is standardised against 0·001 *N* potassium permanganate solution, the end-point being the yellow colour in the colour-change blue—green—yellow. Standardisation by either method gives the same result. Permanganate, ferricyanide and iron may be determined by means of indigo-carmine titrations, and, conversely, indigo carmine itself may be determined. On amounts of potassium ferricyanide varying from 0·8 to 0·016 mg. the results differed from the calculated amounts by less than 2 per cent. Slightly greater errors, up to a difference of 4 per cent., were obtained in determinations in the presence of large amounts of foreign substances. It has been shown (Mika, *Z. anal. Chem.*, 1929, **78**, 268) that the accuracy of the micro-permanganate titration of iron depends on the size of the indicator correction. For a 0·001 *N* permanganate solution this is about 0·12 ml. for a final volume of 5 ml. For indigo carmine it is only 0·03 ml. for a final volume of 5 ml. Therefore it is more accurate than the direct permanganate titration to reduce the excess of permanganate by a known volume of indigo carmine, and to titrate back with permanganate. The

iron may also be determined directly by means of 0·001 *N* indigo-carmine solution and a weak solution of potassium permanganate. Fairly good results were obtained in the determination of very small amounts of iron, varying from 7 to 100γ; on 7γ the error was 20 per cent., and on 15 to 100γ it was of the order of 5 per cent.

J. W. M.

Microchemical Colorimetric Determination of Sodium. A. Elias. (*Anales Asoc. Quím. Argentina*, 1935, **23**, 1–3.)—In this method the sodium is precipitated as the triple acetate of uranium, sodium and magnesium, and the uranium in the precipitate is determined colorimetrically. To prepare the reagent, two solutions are made: (1) 50 g. of uranium acetate are dissolved in 30 ml. of glacial acetic acid and the volume is made up to 250 ml. with water; (2) 165 g. of magnesium acetate are dissolved in 30 ml. of glacial acetic acid, and the volume is made up to 250 ml. (presumably with water). The two solutions are mixed, and the mixture is left for a few days and then filtered. An approximately 2 per cent. sodium salicylate solution is also required. The colour is finally matched against that obtained with 0·1 *N* sodium hydroxide solution.

Of the solution to be tested—which should contain 0·001 to 0·002 g. of Na_2O per ml.—1 ml. is treated in a small beaker with 5 ml. of the reagent. In another beaker 1 ml. of 0·1 *N* sodium hydroxide solution is acidified slightly with glacial acetic acid and treated with 5 ml. of the reagent. Precipitation is induced by rubbing the walls of the beakers rapidly with a glass rod, and the beakers are left for 24 hours in an ice-chest. Each solution is then treated with its own volume of alcohol and, after 20 minutes, is filtered by decantation. The precipitates are washed three or four times with alcohol, the last runnings of which should, after dilution with water, give no reaction with the sodium salicylate solution. The precipitates in the beakers and on the filters are freed from alcohol by means of a current of air and are then dissolved in water to a volume of 50 ml. Five ml. of each are treated with 5 ml. of 2 per cent. sodium salicylate solution and the colour intensities are matched by suitable dilution.

This procedure allows of the rapid determination of sodium in 10 ml. of water, which may need concentration to 1 ml. if the mineral-content is low. Potassium is not precipitated by the reagent if its concentration, as chloride, is below 20 per cent.; precipitation of lithium begins when 11 per cent., as chloride, is present. Free mineral acids should be absent, and any phosphate or arsenate should be removed beforehand.

T. H. P.

Elimination of Phosphoric Acid in Qualitative Micro-analysis. S. Ginsburg and M. H. Pringsheim. (*Bull. Soc. Chim.*, 1935, **2**, 1694–1697.)—The method is based upon the observation of Willstaetter (*Ber.*, 1924, **57**, 1088) that phosphoric acid can be separated from aqueous solutions by means of certain colloids such as aluminium B hydroxide and colloidal ferric hydroxide. The separation may be carried out suitably in a medium of *N*/10 acetic acid. For 10 ml. of a solution of potassium dihydrogen phosphate (0·05 per cent. of P_2O_5) in *N*/10 acetic acid, it is necessary to use 10 ml. of a suspension of colloidal ferric hydroxide containing 6 mg. of Fe_2O_3 per ml., and to shake the mixture for a few minutes at the ordinary temperature. The method can also be used at higher

concentrations; thus, 8 ml., containing 25 mg. of P_2O_5 and 0·5 ml. of glacial acetic acid, were treated with 8 ml. of a solution of colloidal ferric hydroxide containing 120 mg. of ferric oxide, and afterwards with 4 ml. containing 60 mg. of ferric oxide. This procedure effected complete elimination of phosphoric acid. In experiments in which certain other metallic salts (sulphates of nickel, manganese, chromium, aluminium, zinc) were also present, the phosphoric acid was eliminated by the procedure described, except from the solution containing chromium sulphate, with which it was necessary to increase the quantity of precipitant. Zinc phosphate was precipitated only at higher concentrations on addition of $N/10$ ammonium acetate solution. After elimination of phosphoric acid from the solutions containing iron and aluminium sulphates these metallic cations were not present in the solution. Nickel and manganese remained in the solution after the phosphoric acid had been removed. Zinc also remained in solution, but in smaller amount.

A. O. J.

New Test for Phosphate and Arsenate. L. W. Marrison. (*Chem. and Ind.*, 1935, **54**, 872).—One drop of the test solution is placed on filter-paper with 1 drop of sodium sulphide solution ($N/50$). A drop of ammonium molybdate solution (2·5 per cent.) acidified with sulphuric acid is placed near the first drop so that the solutions join. Molybdenum-blue forms instantaneously in the presence of orthophosphate, pyrophosphate, metaphosphate, or arsenate; the limit of sensitiveness is 0·0005 mg. If only small amounts of phosphate are present, the blue can be seen only at the junction of the drops or at the periphery of the brown molybdenum sulphide stain which also forms. Thiocyanate, ferrocyanide and ferricyanide should be absent, or present only in minute proportion compared with the phosphate.

S. G. C.

Physical Methods, Apparatus, etc.

Measurement of Ultra-violet Radiation in Daylight. J. S. Owens. (*Lancet*, 1935, **229**, 589–590.)—The principle used is that of an optical wedge which admits graduated quantities of light through a number of holes in an opaque plate to a sensitive paper. The use of an actual wedge is, however, open to the objection that its optical properties are not permanent, constant and reproducible. The difficulty is overcome by the use of 13 blackened tubes (diameter 0·5 inch) arranged in concentric circles and all the same height (about 6 inches). The tops of the tubes terminate in holes which vary in diameter from 0·7 to 10 mm., but the lower ends are closed by plates, each of which has a hole 3/16 inch in diameter in the centre of the base of the corresponding tube. A No. 14 Chance filter is placed over the top (to ensure that only light between 300 and 400$m\mu$ is transmitted to the apparatus) and a piece of Kodatone paper is held against the underside of the perforated plate at the bottom. On exposure to light, therefore, a number of spots are produced on the paper, and the density of each is proportional to the amount of light received, and this itself is proportional to the area of the corresponding top-hole. The scale is designed for an exposure of one whole day, since the brightest and longest day just gives a spot under the smallest hole, whilst

the dullest or shortest day produces a similar effect through the largest hole. It is only necessary, therefore, to count the number of spots visible after 24 hours, and this number, referred to a scale, gives a measure of the required intensity; the paper should be inspected without fixing, as this causes fading. Advantages are robustness, waterproofness, no necessity for calibration (and this enables results obtained with different instruments to be compared), the personal factor is almost eliminated, and there is no variable wedge. It is preferable to measure only sky-light, and to this end the instrument is mounted at 45° pointing north (or at the zenith in this country). It may, however, be used to measure sunlight, and it is then advisable to use a ground or diffusing surface on the ultra-violet filter. In this connection it is interesting to note that ultra-violet radiation from the sky is often actually increased by the presence of clouds which reflect sunlight. Data are given which demonstrate the rapidity with which the intensity of ultra-violet light, as measured by this instrument, falls off as the instrument is brought nearer a building or tree which cuts off sky-light. J. G.

Photography of Fluorescent Minerals. W. M. Thornton and M. N. Lewis. (*Bull. Soc. Franc. Minéralogie,* 1934, **57**, 268–269.)—The specimen is placed on a black background in a darkened room and illuminated by means of a mercury-vapour lamp at a suitable angle. A filter (*e.g.* Hanovia Sc. 2682) is placed between the lamp and the object to eliminate visible light, and another (*e.g.* Corning Noviol C or Wratten K2) between the object and the camera to allow the passage of the fluorescent light but not the ultra-violet light reflected by the object. The optimum exposure is determined by trial and error. Among other applications in mineralogy the method may be used to examine substances responsible for lack of homogeneity in minerals; to aid investigations on mineralogical composition by planimetric integration; and to facilitate microscopical investigations of structure, especially of polished surfaces. The radioactivity of certain minerals (*e.g.* Mexican samarskite) has been used in a similar way. Photographs illustrate autunite disseminated in porphyry (from Foley Mountain, S. Dakota) in the light of an ordinary incandescent lamp and in ultra-violet light; in the latter case the porphyry only is visible, and appears as bright spots. A zinc mineral (from Franklin Furnace, New Jersey) is also illustrated. In ordinary light two veins (willemite and a rose-coloured mineral, probably manganiferous calcite) appear dirty white, and the remainder of the specimen has the usual appearance of willemite when associated with franklinite. In ultra-violet light the willemite appears green to yellow, and the other fluorescent minerals are rose-coloured; the filter allows the passage of the former, which appears white in the photograph, but absorbs most of the latter.

ABSTRACTOR'S NOTE.—The colour and intensity of the fluorescence of willemite vary considerably according to the locality in which the mineral is found.

J. G.

Reviews

HANDBUCH DER LEBENSMITTEL CHEMIE. Edited by A. BÖMER, A. JUCKENACK and J. TILLMANS. Vol. II, Part 2. Pp. 537–1726. Berlin: Julius Springer. 1935. Price 145 RM. (bound 148.60 RM).*

This substantial volume continues the style of Part I noticed in THE ANALYST (1934, **59**, 440), and treats of chemical and biological methods of general application in relation to nitrogen compounds, serological methods, enzymes, carbohydrates, acids, dyes, poisons, vitamins, bacteriology and mycology. The treatment, though encyclopaedic and abounding in original references, is concise, and shows evidence of discrimination born of experience.

Food chemistry has suffered a severe loss by the untimely death of Prof. Tillmans of Frankfurt, one of the editors of these volumes. Tillmans was a most able active investigator, and many volumes of the *Zeitsch. Unters. Lebensmittel* bear witness to his industry and genius; few men could be better fitted to undertake the production of the great treatise now being issued, and we may perhaps be permitted to offer a sympathetic tribute to the editors at the loss of so distinguished a colleague whose name was esteemed here as well as in Germany. An obituary of Tillmans appears in the *Zeitsch. Untersuch. Lebensmittel*, Vol. 65, at p. 209.

Drs. Bömer, Grau and Täufel contribute the first sections on the determination of the elements and of water; every good method, including micro methods, applicable to foods seems to have been included. Then follows a longer section by Dr. Bömer on nitrogen compounds (including general and specific protein determinations), amino-acids, amines, ammonia, nitrates and nitrites; it is thoroughly up-to-date, and includes recent work on amino acids as well as details such as methods (Pluckers) for determining nitrites and sulphites present together. Professor Griebel follows with a chapter on serological methods; he explains first the theory, then the technique, as applicable to the detection of horseflesh in sausages and the identification of other kinds of flesh and fish. Progress in this branch is slow, and difficulties arising from cooking have yet to be overcome, but the methods are shown to be applicable to milk, plant and egg proteins, as well as to caviare and honey.

Drs. Waldschmidt-Leitz and Balls contribute 120 pages of sound and valuable matter on enzymes. Carbohydrates, by Professor Grossfeld, occupy 130 pages. Methods are given for the determination of every kind of sugar, including pentoses and polysaccharides occurring in foods. But it is surprising that among the many methods cited the elegant and much-used methylene blue process, for which we are indebted to Lane and Eynon, is not given. Perhaps this method and the chloramine-T method are destined to appear in later volumes under particular foodstuffs. Crude fibre, lignin, cutin, pentosans, pectins and glucosides are well treated. Alcohols, aldehydes, including two useful pages on diacetyl, organic acids and the mineral constituents of foods, are dealt with in about 300 pages (by Drs. Bömer and Windhausen), which are packed with useful matter, though we notice some omissions of good methods. In general, the writers have included the

* According to a circular recently received, it appears that a reduction of 25 per cent. has now been made in the export price of this and other German books.

best work from all parts of the world, and the references are to original sources, as well as German abstracts.

The next section is somewhat novel in a book on foods; it comprises 170 pages, from the pen of Professor Gronover, on the detection of poisons. It deals with the examination of food or viscera for metals, organic poisons, alkaloids, ptomaines and drugs. Perhaps it is a sign of the times that there is a chapter on the mathematical treatment of experimental results, showing probable errors; it comes before a section on vitamins and their assay by Messrs. Scheunert and Schieblich. Lastly, there is a good chapter on the bacteriology and mycology of foods by Professor Griebel; this would be even more interesting if it dealt more specifically with food-poisoning and its causes, rather than with general bacteriological technique, for which we are accustomed to turn to special text-books.

The work, as a whole, is extremely thorough and deserves high commendation. The price reduction recently notified is particularly welcome, but, even so, the cost of the series is very much higher than that of the best English and American scientific books. H. E. Cox

ORGANIC SYNTHESES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Vol. XV. Pp. v + 104. Editor: W. H. CAROTHERS. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1935. Price 8s. 6d. net.

This, the latest volume of this series of annual publications, gives directions for the preparation of thirty substances. As is usual, each preparation has been checked independently, and thus one may confidently expect to be able to repeat the results. No change has been made in the mode of presentation.

The substances whose preparations are given in this volume are of more than usual interest; many of them are substances of practical value, whilst the methods used for others are distinctly worthy of study. Among the former class may be mentioned diazomethane, anhydrous hydrogen bromide and dimedone, oleyl alcohol, and among the latter nitrosomethyl urea, *p*-iodophenol, and α-tetralone.

In connection with dimedone—the modern reagent for the detection of aldehydes—it is stated that the product obtained melts at 147° C., whilst in the literature 150° C. is given. In view of this statement, it is curious that no reference is made to the work of the late A. W. Crossley on the preparation of this substance. His method, which employs the same reagents, differs only in detail from that given; but a sample of dimedone made under his direction some 15 years ago still melts at 150° C. (A recently-purchased A.R. sample melted at 147° C., and the formaldehyde condensation products from the two sources also differ slightly in melting-point.)

The volume ends with an appendix containing additions and corrections to work set out in previous publications, and a subject index covering Volumes X to XV. Volume XV being well up to the standard of its predecessors, and also more than usually interesting, may be recommended to all interested in the preparation of organic chemicals. HAROLD TOMS

EINFÜHRUNG IN DIE ORGANISCH-CHEMISCHE LABORATORIUMSTECHNIK. By Dr. KONRAD BERNHAUER. Pp. x + 129. Berlin: Julius Springer. 1934.

This little book, which is very clearly printed in Roman type, is, as its title suggests, an introduction to the laboratory technique of organic chemistry. It is suitable for advanced students and those beginning any form of research needing skill in the manipulation of the apparatus used in the preparation of organic substances. It thus occupies a place between the ordinary text-books of practical organic chemistry and the great reference works.

The subject is not developed in historical order, for this, as is implied in the preface, would have necessitated the inclusion of methods which, although useful in their day, have long since given place to better ones, and the author's endeavour has been to include only methods which are well-tried and tested. Numerous items of sound advice are given to the worker; thus, he is urged to acquire a thorough familiarity with vacuum work in all its aspects.

After a general introduction, dealing with organic reactions and the isolation, purification and characterisation of organic substances, there follow very detailed sections on almost every operation and variation thereof likely to occur in the organic laboratory. In brief, the principal subjects dealt with are:—Section I, general matters concerning heating, cooling and vacuum apparatus; Section II, methods for carrying out reactions classified according to the type of apparatus needed; Section III (which constitutes the major portion of the book) describes methods for isolating and purifying substances, and gives valuable detail of such processes as distillation, evaporation, sublimation, extraction, crystallisation and absorption. The appendices deal with: (i) Glass apparatus; (ii) the handling of corrosive, poisonous and explosive materials; and (iii) the organisation of laboratory work. Lastly, there are some very noteworthy remarks on the art of writing for publication. A comprehensive index is also included.

Dr. Bernhauer's book is a very satisfactory volume. It is up-to-date, for it contains references to 1934 publications and includes an account of the application of adsorption methods for the purification and separation of compounds of definite structure (such as the carotenes) and of enzymes. Micro- and semi-micro methods also receive attention. The book is clearly printed, contains many excellent diagrams and much useful information and is essentially a work for the laboratory and is well worthy of attention. HAROLD TOMS

PLANT PHYSIOLOGY. By MEIRION THOMAS, M.A. Pp. xii + 494; with 75 illustrations. London: J. & A. Churchill, Ltd. 1935. Price 15s.

In the preface the author says "It is true that excellent recent and older works exist, but they are not numerous, and there is still room for several more in which the subject is treated from different standpoints and with different objects in view." He then explains that the present book has been written to assist students who wish to develop the knowledge of plant physiology that they have acquired in general courses on botany, and it is hoped that it will prove useful to students of chemistry, physics, agriculture, and other subjects, as well as to students who are making a special study of botany. It may be said at once that in the reviewer's

opinion this book should go a long way towards achieving the author's purpose. To produce a concise and readable account of plant physiology within the limits allotted is no mean achievement, and great credit is due to the author for the way in which he has selected his material so as to present a reasonably complete picture of present-day knowledge of the subject.

The book is divided into four parts and two appendices: Part I, entitled Protoplasm, consists of three chapters dealing with the living cell as a whole, the physico-chemical heterogeneity of protoplasm, and protoplasm as a chemically active system. Part II deals in ten chapters with the absorption, translocation and elimination of water solutes and gases, with special reference to the physical and chemical principles underlying these phenomena. Part III consists of four chapters concerned with metabolism, photosynthesis and respiration. Part IV is devoted to growth and movement, and contains a commendably lucid and up-to-date account of recent work on hormones. Appendix I gives a brief account of the chemistry of all the more important metabolic products occurring in plants, and Appendix II deals with aspects of physical chemistry. A minor blemish, which, none the less, calls for comment, is the peculiar misprint on page 419 of *Isatia tinctora* for *Isatis tinctoria*.

The book may be confidently recommended as a handy and reliable source of information on the subjects with which it deals. P. HAAS

QUALITATIVE CHEMICAL ANALYSIS. By F. MOLLWO PERKIN. Fifth Edition, revised by Dr. J. GRANT. Pp. viii + 377. London: Longmans, Green & Co., Ltd. 1935. Price 9s. net.

In this new edition Dr. Grant has preserved the general outlines of the original issue, while bringing the subject-matter thoroughly up to date. The classical methods of separation are retained, but the use of modern reagents is fully described wherever applicable—usually in the form of confirmatory tests; for example, the specific organic precipitation reagents for metals. The use of micro-analytical methods is encouraged, and a surprisingly comprehensive series of micro-tests, requiring the simplest of apparatus, is given. The "rarer elements" are adequately dealt with, methods of identification being described under the appropriate group separations.

The organic sections have been amplified to some extent, particularly that on the alkaloids. With reference to the determination of melting-points, the corroborative "mixed melting-point" test might usefully have been mentioned.

Few errors are to be noticed in the text; in paragraph 7 on p. 146, "test for iodine" should read "test for iodide"; on page 227, thiosulphuric acid is mentioned where thiocyanic acid is meant.

In the separation of metals by hydrogen sulphide, students are warned of the tendency of the sulphides of tin and cadmium to be held up by strong hydrochloric acid; the warning might well have been extended to include lead sulphide, precipitation of which is prevented by as little as 3 per cent. of hydrochloric acid. A curious error has crept in on p. 171 concerning the separation of sulphur acids, confusion having arisen from the replacement of $PbCO_3$ in the earlier edition by

$CdCO_3$ in the present issue. In describing the well-known turmeric reaction with boric acid, no mention is made of the necessity to dry the test paper subsequently. These, however, are minor matters, and do not detract from the general excellence of this revision of a deservedly popular text-book. J. U. LEWIN

INFRA-RED PHOTOGRAPHY. By S. O RAWLING, D.Sc., F.I.C. Second Edition. Pp. xii + 66. London and Glasgow: Blackie & Son, Ltd. 1935. Price 3s. 6d. net.

It is not surprising that there has been an early demand for a new edition of Dr. Rawling's compact little guide to infra-red photography, for it happily combines theory with practice in a way that makes an appeal both to the scientific worker and to the amateur photographer.

The general arrangement of the book is the same as in the previous edition, but there is a considerable amount of new matter embodying the results of work done during the past two years. There are now also numerous references to scientific journals and a useful bibliography of papers relating to infra-red sensitising dyes, but there are still many gaps. For instance, there is no mention of Plotnikow's discovery of longitudinal striation and reflex scattering of rays, which affords the best, if not the only satisfactory, explanation of such infra-red phenomena as the resistance of the eye to the heat rays of a tropical sun.

The praise that was given to the first edition (ANALYST, 1933, **58**, 726) may be extended to its successor. Infra-red photography is relatively so simple in technique, and has so firmly established its value in scientific work, that it must be increasingly used in future. Anyone with an elementary knowledge of ordinary photography will find in this book the way of dealing with any difficulties he may encounter when first he attempts to apply his methods in a region beyond the visible spectrum. EDITOR