THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT MEETING with the Food Group of the Society of Chemical Industry was held at the rooms of the Chemical Society, Burlington House, W.1, on February 7th.

In the absence of the President, Professor W. H. Roberts, the chair was taken by Dr. Roche Lynch, and the Chairman of the Food Group, Mr. E. B. Anderson, was also on the platform.

The subject was "Carotene and Allied Substances in Foods and Feeding Stuffs," and the following papers were read and discussed:—"The Constitution and Physiological Significance of Carotene and Allied Pigments," by R. A. Morton, D.Sc., F.I.C.; "The Commercial Determination of Carotene and Allied Pigments, with Special Reference to Dried Grass and other Leafy Materials," by W. M. Seaber, B.Sc., F.I.C.

The following candidates have been elected members of the Society:

Horace George Battye, Ph.D., F.C.I.C., Registered Engineer (Chemical), Ontario.

George Malcolm Dyson, B.A., B.Sc. (Oxon), Ph.D. (Lond.), F.I.C., A.M.I.Chem.E.,Chief Chemist, Genatosan, Ltd., Loughborough, Leicestershire. (*Through North of England Section.*)

Jack Kerfoot, B.Sc., A.I.C., Assistant Chemist, Research Department, L.M.S. Railway Co. (*Through North of England Section.*)

Ada Frances McColl (Miss), A.I.C., Chemist in department of Scottish Co-operative Wholesale Society. (*Through Scottish Section.*)

NORTH OF ENGLAND SECTION

THE Fifteenth Annual General Meeting of the Section was held at Manchester on January 27th, 1940. The Chairman (Professor T. P. Hilditch) presided over an attendance of thirty-two. The President, Professor W. H. Roberts, was present.

At the request of the Chairman the members stood in silence as a mark of respect to the late H. T. Lea.

The Secretary presented the Report and Financial Statement, which were adopted.

The following appointments were made:—*Chairman*, J. R. Stubbs; *Vice-Chairman*, W. G. Carey; *Committee*, H. Childs, H. H. Jones, T. W. Lovett, H. M. Mason, J. G. Sherratt, C. J. H. Stock; *Honorary Auditors*, U. A. Coates, J. W. H. Johnson; *Honorary Secretary and Treasurer*, A. Lees.

The following papers were read and discussed:—"Some Aspects of the Purification of Polluted Waters for Industrial Use," by J. G. Sherratt, B.Sc., F.I.C., and "The Estimation of Lead in Drinking Waters," by C. H. Manley, M.A., F.I.C.

Estimation of Praseodymium and Neodymium in Solution from their Absorption Spectra

By J. NEWTON FRIEND, D.Sc., and DOUGLAS A. HALL, Ph.D.

The absorption spectra of solutions of the rare earths, particularly praseodymium and neodymium, have been studied by many investigators, both in the visible region, when possible, and photographically in the ultra-violet region. One of the most important objects has been the detection and estimation of small quantities of an earth present as impurity in excess of some other earth. This is of special value in atomic weight determinations when earths of exceptional purity are required, while purely chemical methods of separation are either not available or give uncertain results.

The method breaks down when the bands of one element overlap those of another. Thus a neodymium band readily obliterates the most characteristic erbium band, $\lambda = c.5230$, so that the latter earth may be overlooked in presence of only small amounts of neodymium (Driggs and Hopkins[1]). Although a certain amount of overlapping occurs with praseodymium and neodymium, the difficulty may be partly overcome by a suitable selection of the bands to be studied.

In general, three different methods of estimating the rare earths by their absorption spectra in solution have been attempted. Delaunay[2] examined solutions of the nitrates of praseodymium and neodymium, plotting curves to show the relation between the widths of the chief bands in the visible region and the lengths of the absorption tube. These widths were compared with those given by solutions of unknown composition and, on the assumption that Beer's law is obeyed, the concentrations of the salts giving bands or equal widths were taken as inversely proportional to the length of the absorption tube. Panchromatic plates were used, and an accuracy of some 5 per cent. was claimed. A weakness of this as a general method lies in the diffuseness of many bands, especially in dilute solution.

A second method, suggested by Yntema,[3] surmounts this difficulty. It consists in finding the dilution necessary to effect the disappearance of the most persistent band of a given earth in a mixture under rigid photographic conditions and calculating the original concentration from that of the pure rare earth solution which likewise just fails to give the same band under identical conditions. Inoue[4] found that traces of cerium in the presence of a large excess of other rare earths can be estimated with considerable accuracy in this way, using the band with

maximum absorption at 2469Å. We tried this method in the visible region with solutions of neodymium, using the unaided eye instead of photographs. It was found, however, that the eye tired, so that the results were uncertain.

The third and oldest method is based on the Nessler principle and, when confined to the visible spectrum, does not require a camera. It consists in diluting the unknown solution until the intensities of suitable absorption bands appear, by direct vision, to equal those of a standard solution placed in juxtaposition. Both Brauner[5] and Jones[6] used this method in estimating small quantities (up to some 3 per cent.) of praseodymium as impurity in neodymium solutions, and *vice-versa*. This procedure has been widely adopted in estimating traces of these and other coloured earths in modern atomic weight determinations.

All of these methods are based on the assumption that the spectrum is not appreciably affected by the presence of other earths or compounds in the same solution. Inoue[4] stated that this was true of the ultra-violet bands of cerium in presence of excess of other rare earths. But it has long been known that the visible bands of praseodymium and neodymium are materially affected by the nature of the acid radicle present in both position and intensity. Further, the bands of the nitrates are influenced by the presence of other rare earth nitrates, by magnesium nitrate and even by excess of free nitric acid (Quill, Selwood and Hopkins[7]; Selwood[8]). It is true that Inoue[4] denied this in respect of chloride solutions, but no details of his apparatus are given and no data concerning the concentrations and proportions of the added salts. It is impossible, therefore, to gauge the sensitiveness of his procedure. Schaeffer[9] and, more recently, Uzumasa[10] have observed that organic solvents also affect the bands. These results support the destructive criticisms of Baxter and Chapin[11] on the supposed accuracy of the estimation of praseodymium by the third method given above.

When mere traces of impurity are concerned, such as the 0·005 per cent. of holmium in the yttria used in an atomic weight determination (Kremers and Hopkins[12]), an error of even 20 per cent. might still be without influence on the result. But with higher concentrations, such as those used by Brauner and by Jones, mentioned above, a similar percentage error might be serious. No determination of the magnitude of this error appears to have been made. The present research has been undertaken to ascertain the order of accuracy attainable by the third method, using pure solutions of the earths, and also the toleration concentrations of free nitric acid and the nitrates of cerium and magnesium that may be present without appreciably affecting the results. The present study is limited to the nitrates of praseodymium and neodymium, and the results have proved encouraging. The experiments were carried out with a Hilger constant deviation spectrometer illuminated by 40-watt gas-filled opal lamps. The absorption cells were 6 cm. in length and the slit was set at the minimum width to yield a clear spectrum with least eye strain (1·0 on the scale of the Hilger instrument). The concentrations of the rare earth solutions were determined by precipitation as oxalate and ignition to oxide, using the precautions already detailed for neodymium (Friend[13]) and praseodymium (Friend[14]).

NEODYMIUM NITRATE.—It was first necessary to ascertain which of the numerous absorption bands could be most conveniently studied. Three bands

were eventually selected, namely, band Nd1, extending in 3·5 per cent. solution from 5194 to 5240Å; this, on dilution, yielded eventually two lines* at approximately 5216 and 5203Å. The two other bands yielded lines at approximately 5120 and 5085Å, respectively; these are denoted as Nd2 and Nd3. A further band, Nd4, occurred round 5770Å.

Since, with increasing density of an absorption band, small variations in that density become less easy to detect, solutions of various concentrations were tested to determine the conditions of optimum sensitivity. A standard solution was placed in one cell and band Nd1 was matched spectroscopically with the corresponding band of an unknown solution in a second cell of identical dimensions so placed that the two spectra lay in juxtaposition, the one immediately above the other. The matching was carried out in two ways, namely, "from above," that is, by diluting a more concentrated unknown solution until it matched the standard, and "from below," that is, by increasing the concentration of a more dilute solution. The results obtained were as follows:

TABLE I

	$Nd(NO_3)_3$ g. per litre		
	(1)	(2)	(3)
Standard	18·3	34·7	83·2
Matched:			
(i) From above..	18·8	35·1	81·8
(ii) From below ..	18·6	34·7	89·7

From the table it is evident that a suitable concentration is afforded by 30 to 40 g. of neodymium nitrate per litre (0·27 to 0·36 *N*) the error being only about 1 per cent. These concentrations have therefore been used throughout this research.

Nitric Acid.—The effect of this acid was determined by taking 25 ml. of standard neutral neodymium nitrate solution in two similar cells, adding distilled water to one and an equal volume of diluted nitric acid to the other. The densities of the absorption bands were compared after each addition. It was ascertained by analysis that, with the concentrations used, there were no appreciable volume changes on mixing.

With unit free acid normality no difference could be detected in the bands; at 1·16 *N* bands Nd1 and 2 began to fade. At higher concentrations they changed not only in intensity but alse in structure.

In order to determine the order of accuracy attainable by matching neutral and 2·15 *N* acid solutions, bands Nd2 and 3 were compared because Nd1 became too diffuse. Equal band densities were given with:

3·04 per cent. of $Nd(NO_3)_3$ in 2·15 *N* nitric acid.
2·36 ,, ,, ,, neutral solution.

The error was thus 28·8 per cent.

Magnesium Nitrate.—Similar experiments showed that up to a concentration of 0·95 *N* (70·5 g. of $Mg(NO_3)_2$ per litre) there was no perceptible difference in bands Nd1, 2 or 3. With 1·15 *N* nitrate, band Nd1 was slightly blurred and

* The term refers to the wave-lengths of the imaginary lines that represent the centres of the bands (at great dilution).

weakened. This would affect the estimation. Experiments up to 2 *N* showed that, whilst free nitric acid affected both the intensities and positions of the bands, with magnesium nitrate the bands remained in the same positions, but became paler and blurred.

Sodium Nitrate.—Up to normal concentration, *i.e.* 85 g. per litre, this salt exerted no perceptible influence. A slight effect was observed with 1·03 *N*, and with 2 *N* solutions the differences were pronounced.

Cerous Nitrate exerted no perceptible influence up to 0·6 *N* (65·3 g. of $Ce(NO_3)_3$ per litre), but at higher concentrations disturbing effects became pronounced, band Nd1 losing its double structure.

Lanthanum Nitrate.—Band Nd1 retained its double structure up to 1·0 *N* (108·3 g. of $La(NO_3)_3$ per litre), although the intensity of the band was sufficiently weakened at 0·8 *N* to affect the estimation of the neodymium ; at 0·7 *N* (75·8 g. of $La(NO_3)_3$ per litre) the effect was negligible.

The effect of nitrates on the Nd4 band should be recorded. It gained in intensity on addition of nitrates other than neodymium nitrate, whereas Nd1 lost. With 1·0 *N* added nitrate Nd4 was generally darker and 25Å wider than in the pure solution, in which, however, it showed more signs of structure.

PRASEODYMIUM NITRATE.—Similar series of experiments were carried out with solutions of praseodymium nitrate. The most suitable band for study was the one extending from 5980 to 5825Å in 3·86 per cent. solution, yielding on dilution a most persistent line at 5890Å.

As with neodymium nitrate, a suitable concentration was 30 to 40 g. of praseodymium nitrate per litre, with which the matching error was less than 1 per cent. This is shown in Table II.

TABLE II

	$Pr(NO_3)_3$ g. per litre		
	(1)	(2)	(3)
Standard	38·6	24·5	93·1
Matched:			
(i) From above..	38·6	24·3	87·6
(ii) ,, below ..	38·8	24·5	89·0

Nitric Acid.—Addition of nitric acid up to 0·8 *N* (50·4 g. of HNO_3 per litre) had no detectable influence. With 0·9 *N* acid the band weakened appreciably in intensity. Equal band intensities were given with

3·37 per cent. of $Pr(NO_3)_3$ in 2·15 *N* nitric acid.
2·80 ,, ,, ,, neutral solution.

The error was thus 20 per cent.

Magnesium Nitrate could be added up to a concentration of 0·8 *N* without affecting the results. In 1·0 *N* solution the band was distinctly less dense.

Cerous Nitrate.—The toleration limit of cerous nitrate was approximately 0·6 *N*. With 0·7 *N* the band was paler and somewhat blurred.

MIXTURES OF THE NITRATES OF PRASEODYMIUM AND NEODYMIUM.—As praseodymium and neodymium invariably occur together in nature, and cannot be quantitatively separated, it is particularly useful to be able to estimate their

amounts in a mixture. Chemical methods, based on the higher oxygen-content of the black oxide of praseodymium, do not yield reliable results (see Prandtl and Ducrue,[15] and Prandtl and Huttner[16]). Unfortunately, there is considerable overlapping of the absorption bands. Whilst it is apparently impossible to determine directly with any approach to accuracy the amount of praseodymium nitrate in the presence of neodymium nitrate, the latter can readily be estimated in presence of up to 50 per cent. of the former in 4 per cent. solutions, using bands Nd1, 2 and 3. The following results (Table III) were obtained:

TABLE III

	Concentration in g. per litre	
$Pr(NO_3)_3$ taken ..	13·0	19·3
$Nd(NO_3)_3$,, ..	23·5	17·6
found ..	23·6	17·8

The error is of the order of 1 per cent. or less.

SUMMARY.—Using a 6-cm. absorption cell, neodymium and praseodymium nitrates can be estimated separately in solutions of 3 to 4 per cent. concentration with an accuracy of about 1 per cent. by comparing the intensities of suitable absorption bands with those of standard solutions.

The toleration limits of other substances that may simultaneously be present in solution without affecting the results are given in the following table (Table IV), in which, for simplicity's sake, the concentrations are stated to the nearest whole gram.

TABLE IV

	$Nd(NO_3)_3$		$Pr(NO_3)_3$	
	g. per litre	Normality	g. per litre	Normality
HNO_3	63	1·0	50	0·8
$Mg(NO_3)_2$ ..	70	0·95	60	0·8
$NaNO_3$	85	1·0	—	—
$Ce(NO_3)_3$	65	0·6	65	0·6
$La(NO_3)_3$	76	0·7	—	—

In presence of neodymium, praseodymium cannot be estimated in this way; but the former can be readily estimated in presence of up to 50 per cent. of the latter.

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THE TECHNICAL COLLEGE
BIRMINGHAM

December 5th, 1939

The Potentiometric Estimation of Glucose with Potassium Ferricyanide in Sodium Carbonate Solution

By H. T. S. BRITTON, D.Sc., F.I.C., and LESLIE PHILLIPS, M.Sc., A.I.C.

The fact that potassium ferricyanide oxidises glucose in alkaline solution was first observed by Gentele,[1] but it was not until 1923 that Hagedorn and Jensen[2] applied the reaction to the quantitative estimation of glucose. They added the glucose to a solution containing an excess of alkaline ferricyanide and heated on a boiling water-bath for 15 minutes. The excess of potassium ferricyanide was then determined by titration by the potassium iodide and sodium thiosulphate method. Van Slyke and Hawkins[3] estimated the excess of ferricyanide by measuring the volume of nitrogen evolved as the result of the reaction with hydrazine.

Whitmoyer[4] adopted a similar method with the exception that, instead of titrating the excess of ferricyanide, he titrated the ferrocyanide formed on oxidising the glucose in the presence of sodium carbonate. This was done by acidifying and titrating with ceric sulphate, with alphazurine G as an internal "redox" indicator.

The direct potentiometric estimation of glucose has hitherto escaped attention, although Wood[5] has devised a somewhat indirect method based on the extent of the "poising action" (*i.e.* buffer action in regard to the oxidation-reduction process) produced by the equilibrium between ferricyanide-ferrocyanide ions which is set up when a glucose solution is added to an alkaline solution of known concentration of potassium ferricyanide at 100° C.

The work to be described consisted in following the changes in oxidation-reduction potential as glucose is progressively added to an alkaline solution of potassium ferricyanide. Preliminary work appeared to show that sodium carbonate provided the best alkaline medium for the purpose. The titrations were carried out in a boiling water-bath, thereby providing a temperature of 92 to 94° C. in the titration vessel. It was also found that there was no need for the rigid exclusion of air.

Experimental.—The apparatus employed was that already described (Britton and Phillips[6]), and the cell combination was

Pt	$K_3Fe(CN)_6 + Na_2CO_3$ + Glucose	Satd. Sol. of KCl	*N*KCl	*N* Calomel

For the titrations, mixtures of *N* sodium carbonate and 0·1 *N* potassium ferricyanide solutions were used. The volumes of each used (given in brackets); their respective concentrations, together with the concentrations of glucose used as titrant, are given in Table I. The original potassium ferricyanide solution, from which the solutions above were prepared, was analysed potentiometrically with potassium permanganate in sulphuric acid solution.

TABLE I

No.	Concentration of alkaline ferricyanide solution g.-mols. per litre $K_3Fe(CN)_6$	Na_2CO_3	Glucose, g. per litre	Amount of glucose solution required ml.	Mols. of $K_3Fe(CN)$ per 1 mol. of glucose
1	0·0095 (20)	0·36 (50)	1	20·33	5·89
2	0·0095 (20)	0·36 (50)	2	10·13	5·87
3	0·0095 (20)	0·36 (50)	3	6·77	5·89
4	0·0095 (20)	0·36 (50)	4	5·07	5·90
5	0·0003 (5)	0·46 (50)	2	2·57	5·89
6	0·0055 (10)	0·42 (50)	2	5·12	5·89
7	0·0077 (15)	0·38 (50)	2	7·72	5·88
8	0·0110 (25)	0·33 (50)	2	12·83	5·91
9	0·0125 (30)	0·31 (50)	2	15·38	5·92

Figure 1 illustrates some of the titration curves; the numbers by which they are marked refer to the titrations recorded in Table I. As shown by the curves, the potentials set up at the platinum electrode during the initial stage of the titrations were positive with respect to the normal calomel electrode, but as the titrations progressed the platinum electrode became negative. The potentials prevailing during the first stage are governed by the reduction process:

$$Fe(CN)_6''' \longrightarrow Fe(CN)_6''''$$

thus at 90—94° C.

$$E_{Pt} = \epsilon_{Fe(CN)_6''' \longrightarrow Fe(CN)_6''''} - 0{\cdot}073 \log \frac{[Fe(CN)_6'''']}{[Fe(CN)_6''']}$$

which shows that as the concentration of ferricyanide-ions diminishes the potential of the platinum electrode becomes increasingly negative. The advantage of potassium ferricyanide over complex alkaline copper tartrate solutions lies in the fact that the potential range corresponding to this process is not so negative as that for $Cu'' \rightarrow Cu'$.

The completion of the reduction of the potassium ferricyanide present in the various solutions is, as Fig. 1 shows, marked by excellent inflexions extending over 400 millivolts for the more concentrated glucose solutions and over 500 millivolts for the more dilute solutions. This sudden drop in potential usually occurs with the addition of 0·1 ml. of glucose solution. The time required to perform these titrations as far as the end-point inflexion is 20 to 30 minutes. The potentials are readily established (within 1 to 3 minutes), and are reproducible. After the end-point, however, the potentials are more sluggish in their attainment and sometimes require as long as 10 minutes before they become constant. This, however, is immaterial to the analytical value of the potentiometric method.

The last column of Table I shows that in the range of concentrations of the solutions used in these titrations the number of molecules of potassium ferricyanide required to oxidise a single molecule of glucose is sensibly constant at 5·9. When compared with complex copper tartrate solutions, in which approximately 5 mols. of CuO are required, it will be seen that alkaline ferricyanide is a little more effective in its action on glucose, in that it causes the oxidation of glucose to proceed to a

greater extent. It is possible that this is responsible for the fact that the potentials set up after passing the end-point are more negative than with Fehling's solution. These more negative potentials, coupled with the higher potentials before the

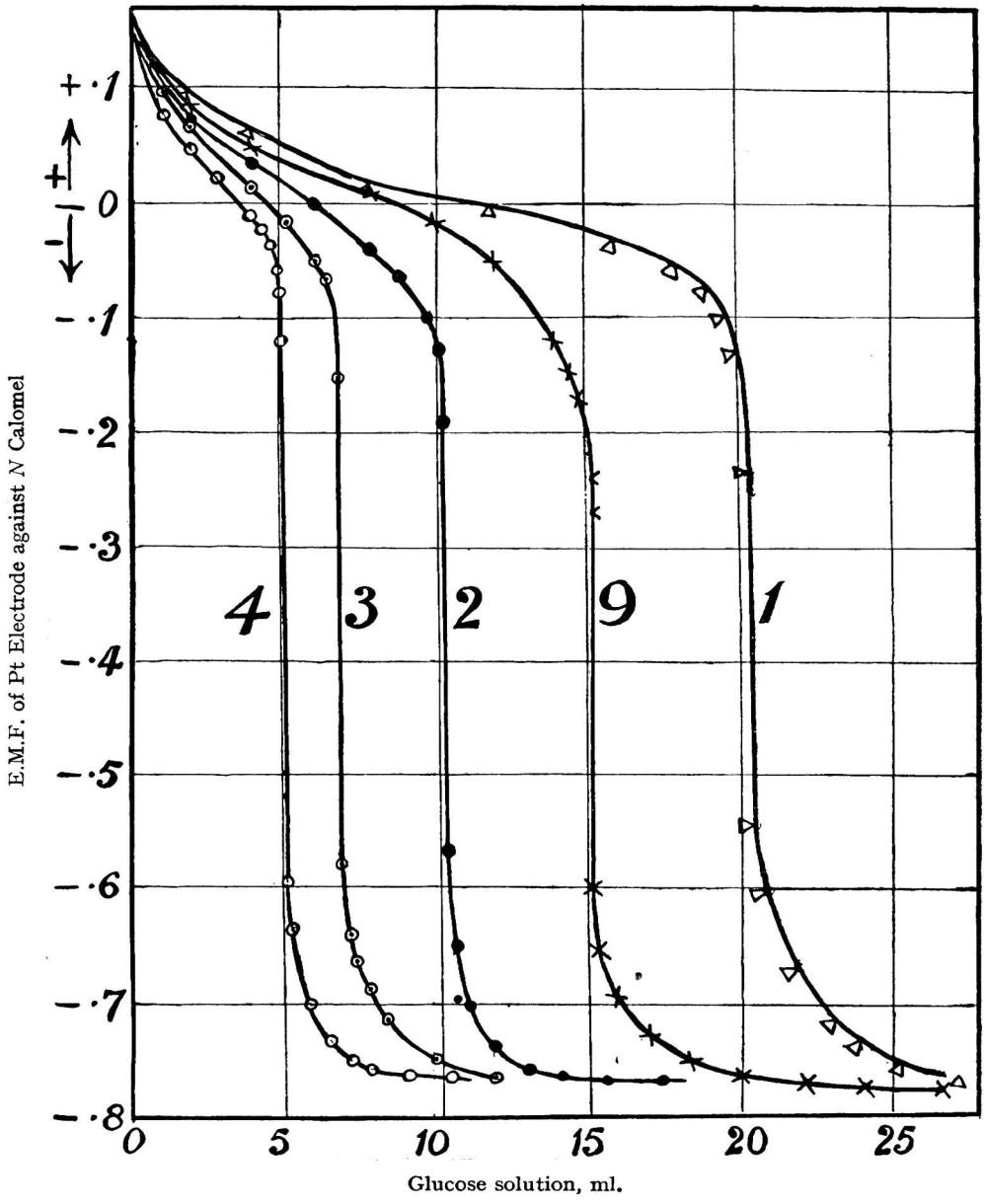

Fig. 1

oxidation of the glucose is complete, give rise to the excellent inflexions obtained and therefore to the greater accuracy of the method, as compared with the Fehling method.

Another point that is brought out by the potentials set up at the end-points and the magnitude of the vertical inflexions is that they pass through the range in which methylene blue becomes decolorised. Methylene blue has been found to be a serviceable internal indicator for titrating sodium carbonate and potassium ferricyanide solutions with glucose at 90 to 100° C. This is being further investigated and will be the subject of a later paper.

One of us (L. P.) wishes to place on record his thanks for the award made to him by the Senate of this College from the Andrew Simons Research Fund.

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WASHINGTON SINGER LABORATORIES
UNIVERSITY COLLEGE
EXETER

July, 1939

A New Test for the Detection of Molybdenum and Tungsten

BY J. HUBERT HAMENCE, PH.D., M.SC., F.I.C.

CLARK has described[1,2] the use of 4-methyl-1:2-dimercaptobenzene (dithiol) for the detection of tin; a reddish precipitate is produced on addition of this reagent to an acidified solution of a tin salt. In the course of some toxicological work I obtained with hydrogen sulphide a reddish-black precipitate which, when tested for tin by dissolving it in conc. hydrochloric acid and treating the solution in the manner described by Clark, yielded a greenish precipitate. Clark, in his paper, describes yellow, black and orange precipitates which are given by some of the more common metals with this reagent, but he does not mention a green precipitate. Further investigation showed this greenish precipitate to be due to the presence of molybdenum.

In view of the possibility that the formation of this greenish precipitate might be specific for molybdenum, salts of all the more common metals were tested with dithiol and, with the exception of tungsten, which produced a light greenish-blue precipitate, no other metal was found to yield a green precipitate.

ACTION OF AMMONIA ON THE METAL DITHIOL COMPLEX.—In the search for another metal that would produce a green dithiol complex, the procedure suggested by Clark, *viz.* the addition of thioglycollic acid and the dithiol reagent to a solution of the metal salt in dilute hydrochloric acid, was extended, and in each instance the effect of the addition of an excess of strong ammonia to the dithiol complex was examined. This additional procedure produced interesting results, in that it was found that all precipitates dissolved readily in an excess of ammonia, producing

nearly colourless solutions, with the exception of molybdenum, which produced a brilliant blue solution. This last reaction therefore gives us a specific test for molybdenum.

ACTION OF THIOGLYCOLLIC ACID.—Another new colour reaction was also observed on addition of thioglycollic acid. Molybdenum ions, if present in the solution, produce a brilliant yellow colour; tungsten, on the other hand, yields no colour. Although this reaction with thioglycollic acid is not specific for molybdenum ions, it serves as a useful confirmatory test.

These two new colour reactions afford a rapid method for the detection of small quantities of either molybdenum or tungsten.

The tests give best results when the quantity of molybdenum or tungsten present in the 10 ml. of solution taken for examination is between 1·0 and 0·02 mg.

PROCEDURE.—Take 10 ml. of the solution to be examined and add sodium hydroxide solution or hydrochloric acid until the mixture is neutral to litmus, add 10 drops of conc. hydrochloric acid followed by 3 drops of thioglycollic acid, and observe the colour produced.

Molybdenum	Tungsten
Bright yellow	Colourless

Add to this solution 1 ml. of the dimercaptobenzene reagent, prepared according to the direction of Clark (*loc. cit.*), boil for 3 or 4 minutes, and observe the colour of the precipitate.

Molybdenum	Tungsten
Dark green precipitate	Light greenish-blue precipitate

Cool the mixture and add an excess of 0·88 ammonia.

Molybdenum	Tungsten
Bright blue	Colourless

By this test, 0·02 mg. of molybdenum in 10 ml. of solution may be detected and a similar quantity of tungsten will give a distinct greenish-blue dithiol complex.

When a suspension of the molybdenum complex in dilute hydrochloric acid is shaken with a mixture of equal parts of amyl alcohol and ethyl ether the complex dissolves in the ethereal mixture, with the production of an olive-green layer. The tungsten complex behaves similarly, yielding a blue layer.

The presence of traces of iron will interfere in the final stage of the test for molybdenum by producing on the addition of ammonia a violet colour with the thioglycollic acid present. Iron, if present, should therefore be removed by pouring the solution to be tested into an excess of sodium hydroxide solution, filtering off the precipitated ferric hydroxide, and testing the filtrate as previously described.

DETECTION OF TUNGSTEN IN PRESENCE OF MOLYBDENUM.—Tungsten may be detected satisfactorily, provided that the molybdenum is first removed by precipitation with hydrogen sulphide. The following experiment indicates the procedure that has been found quite satisfactory:—To 20 ml. of a solution containing 10 mg. of molybdenum and 0·1 mg. of tungsten, and made just alkaline to litmus by addition of sodium hydroxide solution, were added 2 g. of tartaric acid and 0·2 ml. of conc. sulphuric acid. The mixture was warmed to

60° C. and hydrogen sulphide gas was passed through it. The reddish-black precipitate was filtered off, the clear filtrate was evaporated to dryness, and the residue was gently ignited to destroy the tartaric acid. The residue was dissolved in a few drops of 20 per cent. sodium hydroxide solution, and the solution was diluted and examined by the method previously described. A distinct greenish-blue dithiol precipitate was obtained which dissolved in ammonia, giving a colourless solution, thus indicating the presence of tungsten and the absence of molybdenum.

It was found during the experiments on the separation of molybdenum and tungsten by this method that the presence of considerable quantities of tartaric acid or tartrates inhibited the dithiol reaction for tungsten; hence the necessity for destroying the tartaric acid before applying the test.

The method of storing the 4-methyl-1:2-dimercaptobenzene (dithiol) reagent suggested by Clark, *i.e.* in an atmosphere of hydrogen gas, has been found to be very satisfactory, and by this means the reagent may be kept for as long as 3 or 4 months without deterioration.

I wish to thank Dr. Bernard Dyer and Mr. George Taylor for their interest in this work.

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November 4th, 1939

Bleach Ointments

BY D. D. MOIR, M.Sc., F.I.C.

IN view of the importance of bleaching powder preparations in the first-aid treatment of mustard gas casualties, the following notes and observations on the strength and keeping properties of bleach ointment may be of interest.

According to A.R.P. Handbook No. 2, 3rd edition (*"First Aid and Nursing for Gas Casualties"*), bleach ointment consists of equal parts of bleaching powder and white petroleum jelly. Handbook No. 3, 1st edition (*"Medical Treatment of Gas Casualties"*), specifies "supertropical" bleach. For either preparation it is reasonable to expect that the available chlorine in the bleaching powder should not fall below 30 per cent. (the B.P. limit); it is usually higher in powders stored under good conditions. Thus, bleach ointment, when freshly prepared, should contain about 15 per cent. of available chlorine. No specification is given for the white petroleum jelly in the Handbooks, although it is understood that there is an official Specification available to manufacturing chemists, but not generally published. The nature of the petroleum jelly used is, I believe, of the greatest importance. A yellow petroleum should not be used, since there may be interaction between the bleaching powder and the jelly, which can become very vigorous and has been known to cause a fire in large bulk. Even with white petroleum jelly this possibility is not entirely excluded.

The fact that bleach ointment is liable to deteriorate has been known for some time. Chambers and Savage,[1] who prepared bleach ointment according to the earlier A.R.P. formula of two-thirds bleaching powder and one-third petroleum jelly, observed a loss in available chlorine of about 50 per cent. in 15 months. Of this loss, a small proportion was found as combined chlorine in the petroleum base, but by far the greater part had been converted into inorganic chloride.

DETERMINATION OF AVAILABLE CHLORINE.—After several preliminary trials the following method of determining available chlorine was found to be most satisfactory and was used throughout these experiments:—About 1 g. of ointment is weighed directly into a weighed stoppered flask of about 200 ml. capacity. Twenty ml. of carbon tetrachloride are added, and the flask is rotated gently, with slight warming if necessary, until the whole of the paraffin is dissolved; 100 ml. of water are added and the flask is shaken vigorously. About 2 g. of solid potassium iodide are added, followed by 5 ml. of 33 per cent. v/v acetic acid. After a further shaking, the liberated iodine is titrated with $N/10$ sodium thiosulphate solution. Vigorous shaking is sometimes necessary towards the end of the titration to decompose small particles of bleaching powder and to remove the iodine from the tetrachloride. Carbon tetrachloride was chosen because it is a good solvent for the petroleum jelly and is inert towards bleaching powder. The unsuitability of petroleum spirit was emphasised by Chambers and Savage, who showed that it was not without action on bleaching powder. I have not found any definite indication of loss of chlorine from the use of petroleum spirit, but the use of carbon tetrachloride avoids this possibility.

The petroleum base is determined by extraction with petroleum spirit in a Soxhlet thimble lined with filter paper; thus determined it would include any small quantity of chlorine which has entered into combination with the jelly.

I have examined about 40 bleach ointments, mainly taken from pharmacists in the ordinary course of Food and Drugs sampling, and two ointments have been prepared in the laboratory and assayed for available chlorine from time to time. The results are shown in Tables I to III.

Deficiency in available chlorine in a bleach ointment may be due to one or more of several causes. The wrong proportion of bleaching powder may have been used, or the bleaching powder may have been deficient in strength. Deterioration may have occurred either through interaction between the bleaching powder and unsaturated compounds in the petroleum base or by loss in strength of the bleaching powder itself. Any combination of these causes is possible, and it is not easy to distinguish between them.

ANALYSES OF BLEACH OINTMENTS.—The results of analysis can conveniently be classified under the following headings:

1. Ointments correctly prepared and of approximately correct strength (Table I).
2. Ointments deficient in available chlorine (Table II) owing to insufficient bleaching powder (Group 1), or to deterioration before or after preparation (Group 2), or to a combination of these causes (Group 3).

TABLE I

Sample No.	Available chlorine: On receipt Per Cent.	Available chlorine: After time stated in brackets Per Cent.
B 103	14·7	14·4 (8 weeks)
		14·2 (17 ,,)
B 104	15·3	14·8 (8 ,,)
		14·8 (17 ,,)
B 107	12·9	11·6 (8 ,,)
		10·3 (17 ,,)
B 110	16·4	13·1 (17 ,,)
B 113	14·0	13·3 (17 ,,)
B 120	13·9	11·7 (16 ,,)
C 319	14·9	14·6 (16 ,,)
C 321	13·7	11·6 (16 ,,)
C 322	15·3	13·5 (16 ,,)
D 373	13·3	13·0 (15 ,,)
C 355	14·2	11·5 (13 ,,)
C 356	18·9	16·3 (13 ,,)
B 127	13·6	11·6 (12 ,,)
B 129	15·6	14·9 (12 ,,)
D 432	14·9	14·4 (12 ,,)
D 433	15·5	13·5 (12 ,,)
B 131	14·7	14·2 (12 ,,)
E 17	15·2	13·5 (11 ,,)
E 19	14·3	13·3 (11 ,,)
R 101	13·8	13·2 (9 ,,)
C.P. 24	13·7	13·4 (9 ,,)

TABLE II

	Sample No.	Petroleum jelly Per Cent.	Available chlorine: On receipt Per Cent.	Available chlorine: After time stated in brackets Per Cent.	Available chlorine expressed as percentage of the bleaching powder present on receipt
Group 1	B 109	62·3	10·8	8·7 (17 weeks)	28·6
	B 115	89·5	3·7	1·8 (17 ,,)	35·2
	B 121	93·4	2·3	1·3 (16 ,,)	34·9
Group 2	B 114	52·1	11·5	7·5 (17 ,,)	24·0
	C 320	52·5	7·4	6·9 (16 ,,)	15·6
	C 353	52·5	7·7	6·3 (13 ,,)	16·2
	B 132	49·4	3·9	3·9 (12 ,,)	7·7
	B 133	45·6	8·3	7·7 (12 ,,)	15·3
	E 18	52·3	8·9	7·8 (11 ,,)	18·7
	R 95	50·5	10·6	9·3 (9 ,,)	21·4
	R 98	52·6	9·6	7·7 (9 ,,)	20·3
	R 100	48·8	8·1	4·9 (9 ,,)	15·8
Group 3	B 108	56·8	10·3	7·0 (17 ,,)	23·8
	B 111	66·0	1·6	1·0 (17 ,,)	4·7
	B 112	67·9	8·2	5·7 (17 ,,)	25·5
	C 318	67·8	8·2	6·1 (16 ,,)	25·5
	D 372	57·0	7·7	6·2 (15 ,,)	17·9
	D 374	70·2	8·2	7·3 (15 ,,)	27·5
	C 354	56·9	11·0	10·3 (13 ,,)	26·0

Of a total of 40 ointments examined, 21 were passed as satisfactory (Table I). The average available chlorine-content was 14·8 per cent. After periods of about 3 months, or more, the available chlorine had not in any instance fallen below 10·3 per cent. and averaged 13·3 per cent.

Samples Nos. B 104 and C 321 were from different vendors, but had been prepared by the same manufacturer; similarly with D 432 and E 17 and with C 319, B 129 and C.P. 24. It would seem, therefore, that manufacturers are able to prepare consistently bleach ointment of good strength and excellent keeping properties.

In Table II, B 115 and B 121 are informal and formal samples respectively from the same vendor. They were both prepared immediately before sale with a high-grade bleaching powder. The reduction in available chlorine on keeping is considerable, as is to be expected with such a low proportion of bleaching powder relative to the petroleum jelly.

The serious deficiencies in available chlorine of the samples listed in Table II, Group 2, which had the correct proportions of bleaching powder and petroleum jelly, can only be readily explained by assuming a long period of storage or the use of bleaching powder deficient in available chlorine. Several of the ointments were known to have been of recent preparation. The use of an unsuitable white petroleum jelly of high initial reactivity is not entirely ruled out, and is beyond the control of the vendor, who is unable to obtain the official Specification.

Sample No. R 100 gave on extraction with petroleum spirit a sticky residue instead of a dry powder. It was found to contain a considerable proportion of moisture, and it is probable that the bleach had been made into a paste before incorporation with the jelly.

TABLE III

LOSS OF AVAILABLE CHLORINE IN BLEACH OINTMENTS PREPARED IN THE LABORATORY.—*No.* 1.—Prepared with equal parts by weight of bleaching powder and white soft paraffin, both of which were taken from ordinary laboratory stock. The bleaching powder contained 30·0 per cent. of available chlorine, and the ointment should therefore have contained 15·0 per cent. exactly.

No. 2.—Prepared with equal parts by weight of bleaching powder and white petroleum jelly. The bleaching powder was taken from a freshly-opened tin direct from the suppliers, and the white petroleum jelly was also freshly purchased, but without any indication that it was suitable for use in this preparation. The bleaching powder contained 34·1 per cent. of available chlorine, and the ointment should therefore have contained 17·0 per cent.

No. 1		No. 2	
Time	Available chlorine Per Cent.	Time	Available chlorine Per Cent.
Immediately	14·2	Immediately	16·5
After one week ..	13·6	After three weeks ..	13·3
,, two weeks ..	13·2	,, six weeks	11·9
,, three weeks ..	12·7	,, twelve weeks ..	11·6
,, fifteen weeks ..	10·6	,, fourteen weeks ..	11·5
,, seventeen weeks..	10·5		

At the end of these periods the bleaching powders with which the ointments were prepared contained 29·6 per cent. and 33·7 per cent., respectively, of available chlorine.

In both instances there was an immediate initial loss during preparation followed by a fairly rapid decrease in strength for the first few weeks. After about six weeks this loss became every slow.

Ointment No. 2 developed a yellow colour on keeping, although it was in the dark. As measured in the Lovibond Tintometer, the colour developed was equivalent to 1·6 yellow units in a period of two months. The figure was not increased after a further six weeks' storage. This phenomenon was unexpected in presence of available chlorine, but it was also observed in several of the ointments received under the Food and Drugs Act. Nos. B 108, B 115, B 121, B 127, B 132 and R 98, after storing, all had a slight yellow colour similar to that obtained with laboratory preparation No. 2. With one or two ointments which had been stored in cardboard boxes the yellow colour appeared to be more intense on the surface than underneath. This was particularly noticeable in B 126—an informal sample not listed above. The yellow colour developing on the surface of the ointment exposed to the air measured 8·0 yellow units after 3 months, whereas the formal sample, B 132, which was stored in an amber-glass jar with an air-tight screw cap did not exhibit this surface intensification.

These observations constitute a warning against condemning an ointment as having been prepared with yellow petroleum jelly instead of white, as judged by the colour alone. Nos. B 114, C 318 and E 18 were all strongly yellow in colour. No. E 18 was a sample taken from a large batch which had been supplied to a local authority over a year previously. It was believed to have been white when received.

Legal proceedings were taken against the vendors of samples Nos. B 111 (Table II, Group 3) and B 121 (Table II, Group 1), and reports appeared in THE ANALYST, 1940, p. 30. Both were extreme cases in which the available chlorine had reached such a low figure that the article was considered almost useless for its purpose. The cases were dismissed, but it is significant that the Chairman of the Bench at Sutton Police Court said "that a very useful purpose had been served by the case, for now the general public and druggists would know that something was advised in the air-raid precautions handbook which might be regarded as a standard and which it would be wise to keep to, at least until something more authoritative was found."

It is considered that a purchaser of bleach ointment for A.R.P. purposes is entitled to receive an article containing approximately 15 per cent. of available chlorine. It has been shown that in every instance when such an article has been sold the ointment has retained a high proportion of the active ingredient over a period of months and that subsequent deterioration is likely to be very slow.

REFERENCE

1. W. P. Chambers and F. M. Savage, *Pharm. J.*, 1938, **87**, 113.

ANALYTICAL LABORATORY
16, SOUTHWARK STREET
LONDON, S.E.1

January 24th, 1940

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 SIMPLE TEST FOR ARSENIC IN LEAD ALLOYS

THE following limit test for arsenic in lead alloys, mainly those containing between 5 and 20 per cent. of antimony, has been devised in this laboratory. For this purpose the test has proved very useful, and, since it is simple and rapid, it may be of service in other connections.

Two g. of the alloy are heated in a 250-ml. conical flask with about 3 g. of anhydrous sodium sulphate and 15 ml. of conc. sulphuric acid, the contents of the flask being kept in motion to avoid local over-heating. The heating is best carried out over a large Bunsen flame by the use of flask tongs, and is continued until the lead salts appear almost white. After cooling, 75 ml. of water are added, sodium salts are dissolved by gently warming to the boiling-point, and the solution is treated with 75 ml. of strong hydrochloric acid, followed by 2 drops of saturated mercuric chloride solution and 3 ml. of hypophosphorous acid (sp.gr. 1·135). On heating the mixture to the boiling-point with frequent agitation, all lead salts dissolve, and, if arsenic is present in sufficient amount, a brown colloidal precipitate is produced.

As little as 0·005 per cent. of arsenic in the sample (0·1 mg.) gives a colour that is readily perceptible, and no interference is caused by 20 per cent. of antimony, or by any amounts of copper, silver, bismuth or tin that I have met with in antimonial lead. In absence of iron, which is seldom present, an amount of copper of the order of 0·03 per cent. or more is shown by the yellow colour of the warm hydrochloric acid solution, but the colour is discharged when hypophosphorous acid is added. The behaviour of selenium and tellurium is under investigation.

The precipitation of metallic arsenic by hypophosphorous acid in hydrochloric acid solution is well known,[1] but in the present test the sensitivity appears to be considerably enhanced by the small addition of mercuric chloride. Not more than 2 drops of the saturated solution should be used, as there is then likely to be some confusion with the grey colour of precipitated mercury.

Evans[2] used mercuric chloride to catalyse the reduction of tin by hypophosphorous acid, and it is from his paper that the suggestion of the present method arose. There is no doubt that mercuric chloride also considerably accelerates the reduction to metallic arsenic, the effect being more significant when the concentration of the latter element is small.

R. G. ROBINSON

REFERENCES

1. B. S. Evans, ANALYST, 1931, **56**, 523.
2. —— *id.*, 1931, **56**, 170.

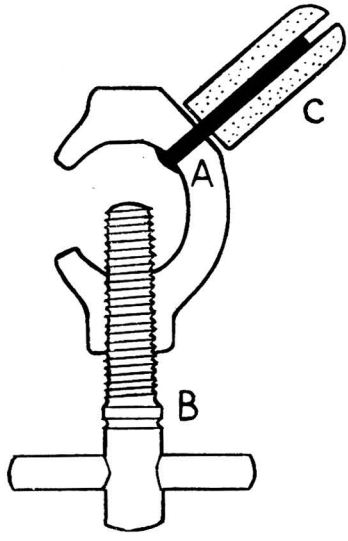
BRITANNIA LEAD CO.
NORTHFLEET

December 7th, 1939

AN ADJUSTABLE SUPPORT FOR CRUCIBLES AND DISHES

IT often happens that platinum dishes and crucibles are heated on pipeclay or silica triangles even in laboratories where thermostatically controlled muffles are available, the muffles being reserved for certain types of work. The following support has been devised and possesses several distinct advantages.

The support is made from small retort bosses which are cut in half, three halves being required for each set. The halved retort boss is drilled with a 5/64 inch hole at A at approximately 45° with the screw B. The boss is filed flat at A at the same angle. A 5/64 inch wire or nail is thickened at one end and inserted from the inside where it is riveted in position. The wire is allowed to project $\frac{3}{4}$ inch and is fitted with a piece of pipeclay from a triangle or with silica tubing of similar size.



Three of these prepared attachments are fastened on the three sides of a triangular tripod with the screw B on the under side or pointing outwards, and with C pointing towards the centre and upwards. By fastening in the centre of the sides, the position is given for holding the smallest crucibles; when each is moved in the same direction along the side, *e.g.* to the left, the distance between the points can be increased as desired to take large dishes. The points should be arranged as far apart as practicable, so that the dish is held by its sides.

The device has the following advantages:—(1) The crucible or dish is supported on three points and the increase in temperature is very appreciable. (2) The points can be readily removed for cleaning or renewal. (3) The device is easily adjustable and takes any size. (4) The crucible or dish is held rigidly and the stand can therefore be moved or rotated safely if desired. (5) The increase in efficiency means a saving in gas. (6) The support is cheap to make (about 1s. 6d.). (7) Where expense is of secondary importance platinum wire can replace the iron wire and can be used direct for supporting the crucible. The ends of the wire should then be bent to prevent denting the crucible.

I wish to thank Messrs. Cadbury Bros., Ltd., for permission to publish this note.

H. C. LOCKWOOD

CHEMISTS' DEPARTMENT
BOURNVILLE

September 25th, 1939

Official Appointments

THE following Notification of Amendment (dated December 16th) of the List of Public Analysts appointed by Local Authorities with the approval of the Minister of Health has been received from the Ministry.

Authority	Name of Public Analyst
NUNEATON BOROUGH	F. G. D. CHALMERS
HARROGATE BOROUGH	F. W. M. JAFFÉ
COULSDON AND PURLEY U.D. ..	E. HINKS
,, ,, ..	D. D. MOIR (Deputy)
WIMBLEDON BOROUGH	E. HINKS
,, ,, ...	D. D. MOIR (Deputy)
WINDSOR (NEW) BOROUGH ..	J. H. WEBER (Deputy)
DARTFORD BOROUGH	F. W. F. ARNAUD
CREWE BOROUGH	T. R. HODGSON
STRETFORD BOROUGH	G. H. WALKER
BECKENHAM BOROUGH	J. W. FLINT (Deputy)
SWINDON BOROUGH	R. H. ELLIS
TORQUAY BOROUGH	THOMAS TICKLE
,, ,, ...	C. V. REYNOLDS (Deputy)
BATTERSEA MET. BOROUGH ..	A. H. M. MUTER (Deputy)
MERTON AND MORDEN U.D. ..	E. HINKS
,, ,, ..	D. D. MOIR (Deputy)
BROMLEY BOROUGH	J. W. FLINT (Deputy)
SCUNTHORPE BOROUGH	JOHN EVANS
WANSTEAD AND WOODFORD BOROUGH	B. DYER, G. TAYLOR } Joint Public Analysts
COLNE BOROUGH	F. MAUDSLEY
WIDNES BOROUGH	J. R. STUBBS

ERRATUM.—In the list of Official Appointments on p. 27 of this volume, the last line, *viz.* LINCS. COUNTY, should be deleted.

Sugar for Chemical Purposes

PERMITS to purchase from a retailer sugar for chemical purposes may be obtained by application to the local Food Control Office. The appropriate form to be completed is numbered P.S.M.1.

Department of Scientific and Industrial Research

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY*

ANILINE VAPOUR

OCCURRENCE.—Aniline exists in small quantities in coal tar, but is produced industrially almost exclusively by the reduction of nitrobenzene. It is used chiefly as a starting point in the manufacture of dyestuffs and to a less extent in other chemical industries. Its pleasant smell in no way suggests the dangers resulting from its presence in the atmosphere.

POISONOUS EFFECTS.—It has been shown that cases of acute aniline poisoning arise by absorption through the skin by splashes either directly on the skin or indirectly through the clothing. Its immediate toxic effect is on the blood, and the symptoms that characterise it are a blue-grey discoloration of the lips, ears and cheeks. Depending on the intensity of the concentration, shortness of breath, rapid feeble pulse, and nervous excitement, not unlike drunkenness, may occur later. With a concentration of 1 part in 140,000 of air, slight symptoms may occur after several hours' exposure, while with concentrations of 1 part in 10,000 to 1 part in 6000 serious disturbance occurs if the atmosphere is inhaled for more than an hour.

METHODS OF DETECTION.—In order to test for the presence of aniline vapour in the atmosphere, the aniline must first be brought into solution by drawing a sample of the air under examination by means of a hand-pump through a small bubbler containing dilute hydrochloric acid. Any aniline vapour present is thereby converted to the hydrochloride, to which any of the ordinary tests for aniline may then be applied.

Normally, however, the concentration of the vapour present in the atmosphere is so small that only very little hydrochloride is obtained without taking an inconveniently large sample of air; several of the ordinary tests are therefore insufficiently sensitive. For example, the best known test for aniline is by adding a few drops of a dilute solution of bleaching powder, which produces a purple colour, rapidly changing to a dirty red; over the range of concentrations of aniline vapour likely to be encountered in the atmosphere, however, only the slightest trace of colour is obtainable.

THE BLEACHING POWDER TEST.—A more sensitive test has therefore been developed from the bleaching powder test. If, after the addition of the bleaching powder, the solution is made alkaline with ammonia and a dilute aqueous solution of phenol is added, a permanent deep blue colour is produced, even with minute quantities of aniline. This test has been adopted as the standard test for aniline vapour in industry. It has been made quantitative by comparing the colours obtained at known concentrations with a series of standard colours prepared from a dye. In this way a table has been drawn up showing the depth of colour obtained with up to 10 strokes of the standard hand-pump over a range of concentrations from 1 part in 5000 to 1 part in 100,000. The table is included in the Leaflet with full instructions for making the tests and for the preparation of the standard colours.

* Leaflet No. 11. H.M. Stationery Office, York House, Kingsway, London, W.C.2. December, 1939. Price 3d. net.

FOREST PRODUCTS RESEARCH BOARD

REPORT FOR THE YEAR 1938*

AN outline is given of the activities of the Laboratory in investigational, educational and advisory work.

IDENTIFICATION OF TIMBER.—About half of the numerous enquiries were concerned with the identification of timber. A representative collection of specimens of softwoods has been made, and from the examination of all characteristics of diagnostic value a multiple-entry card-key (illustrated in the Report) has been devised.

EFFECT OF CHANGES OF MOISTURE-CONTENT OF WOOD.—Investigations of the methods of treating timber to prevent swelling or contraction through changes in its moisture-content have been made. So far, the best results have been obtained by soaking the wood in a solution of sorbitol. In experiments with green beech boards ($\frac{1}{2}$ in. thick) it was found that movement was appreciably reduced when a fairly high concentration (15 to 20 per cent. by weight) of sorbitol was present. The results obtained with oak boards (1 in. thick) were still better. The presence of about 40 to 50 per cent. (by weight) of sorbitol reduces the movement by 40 to 50 per cent.

ABSORPTION OF MOISTURE.—The rates of absorption of moisture by oak, mahogany, teak, red deal, white deal and British Columbian pine, when stored in a damp situation (25° C., 90 per cent. humidity), are given in the form of a graph.

When dry timber is stored for long periods, or alternatively when air-dried timber is to be further seasoned to make it suitable for indoor use, it is very desirable that the storage conditions should correspond, as far as possible, to a moisture-content of about 12 per cent. In a climate with high humidity, as in this country, the required conditions can generally be attained by slight heating. A simple apparatus has been devised for automatically controlling the air conditions in a store. A block of wood is first conditioned to the desired moisture-content and adjusted so that its expansion, as a result of increase of the moisture in the block, closes a switch which brings the heating apparatus into play. The rise in air temperature lowers the humidity, thus causing the wood block to dry and shrink and so break the electric contact at the switch.

FIRE RESISTANCE OF TIMBER.—More than 70 different species have been tested by the laboratory standard methods of determining inflammability, resistance to flame penetration and rate of burning. Those showing outstanding resistance to fire were: Greenheart (*Ocotea rodioei*), gurjun (*Dipterocarpus* spp.), jarrah (*Eucalyptus marginata*), laurel (*Terminalia tomentosa*), padauk (*Pterocarpus macrocarpus*), pyinkado (*Xylia dolabriformis*), teak (*Tectonea grandis*), and white olivier (*Terminalia obovata*).

ACTION OF FIRE-PROOFING COMPOUNDS.—Previous work has shown that the main action of a fire-retarding chemical is its influence on the heated wood, which results in the formation of charcoal at the expense of the production of inflammable gaseous compounds. Further work has confirmed the conclusion that the most effective chemicals are those dissociated by heat, with liberation of an acid radical. Thus, the products from the heating of wood at 450° C. contained 26 per cent. of charcoal, 33 per cent. of condensable organic vapours and 19 per cent. of water; those from the wood after treatment with a 20 per cent. solution of ammonium chloride contained: charcoal, 48; condensable organic vapours, 9; water, 35 per cent. The increase in water vapour also has an effect.

A NEW PRESERVATIVE MIXTURE.—Laboratory tests have indicated that the presence of potassium or sodium dichromate often enhances the leaching resistance of water-borne toxic preservatives. Arising from these tests a new wood preservative mixture has been devised. The addition of potassium dichromate to

* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1940. Price 1s. 6d. net.

mercuric chloride solution resulted in the fixation of the mercury in the wood; under severe test conditions less than 5 per cent. of the mercury was leached out of the treated wood.

CONTROL OF *LYCTUS*.—The principal work on the control of *Lyctus* (powder-post beetles) has been concerned with the investigation of methods of reducing the starch-content of timber.

Estimation of Starch in Timber.—The standard method adopted consisted in treating a clean-cut radial longitudinal surface with a 0·5 per cent. solution of iodine in potassium iodide and estimating visually the amount of starch in each 1/10 inch of wood from the outside of the tree inwards as falling into one of an arbitrary series of grades.

DETECTION OF WOOD-BORING INSECTS BY MEANS OF X-RAYS.—It has been found that, although the presence of insect tunnels can be discovered by X-ray examination, the method is likely to be restricted to timber of small dimensions, such as plywood. It has not proved successful for detecting the death-watch beetle and its larvae in structural timbers.

DESTRUCTION OF INSECTS IN WOOD BY FUMIGATION.—In test experiments exposure, in a commercial fumigation chamber, of the infested wood to the vapours of hydrogen cyanide for 4½ hours at 70° F. killed most, if not all, of the larvae.

PHYSIOLOGICAL STUDIES OF WOOD-DESTROYING FUNGI.—Those fungi that produce a brown rot (*i.e.* attack cellulose and carbohydrates only) cause the medium to become and remain very acid, whilst those that produce a white rot cause an initial development of acidity which disappears after some weeks. The reason for this difference is under investigation.

OTHER INVESTIGATIONS.—Other work described in detail in the Report includes the successful manufacture of charcoal in portable kilns, the effect of repeated applications of oil to wood flooring, the drying of timber by high frequency electric fields such as those produced by radio transmitters, box-testing, the application of statistical analysis to wood bending, and vibration methods for measuring the elastic constants of wood.

Queensland

ANNUAL REPORT OF THE GOVERNMENT ANALYST TO JUNE 30TH, 1939

IN his Annual Report Mr. F. E. Connah, F.I.C., gives a summary of the work done for various departments. The 14,911 samples analysed included 7510 for the Health Department, 2616 for Customs, 1404 for the Postmaster, and 1081 for the Geological Survey. Of the samples for the Health Department, 3349 were taken by inspectors under the Health Act; 2841 of these were passed as satisfactory.

LEAD IN CRAYONS.—Of the 1018 samples examined, 145 were rejected. The amounts of lead in legal samples were: Green (23), 0·1 to 20·4 (aver. 4·0); yellow (19), 0·1 to 14·0 (aver. 2·6); orange (7), 0·2 to 13·0 (aver. 5·4); brown (4), 1·4 to 6·0 (aver. 2·6); red 0·2 to 2·0 (aver. 0·8) per cent. Some black crayons also contained lead (0·9 to 2 per cent.). Most of the lead was soluble in 0·25 per cent. hydrochloric acid.

PARAFFIN OIL ON CURRANTS AND RAISINS.—Seven samples of currants (average water-content 18 per cent.) yielded 0·04 to 0·2 per cent. of ethereal extract. Raisins (7 samples with average water-content 17 per cent.) yielded 0·06 to 0·4 per cent.; 21 samples of sultanas (average water-content 16 per cent.) yielded 0·08 to 0·6 per cent. Any excess of ethereal extract over 0·1 per cent. may be accepted as due to paraffin oil. It is suggested that 0·1 per cent. might be taken as a desirable limit.

COMPOSITION OF "SPECIAL" COFFEES.—Ten samples of "special" coffees sold by local coffee inns gave the following results:

	Mocha Per Cent.	Kenya Per Cent.	Boengi Per Cent.	Java Per Cent.	Costa Rica Per Cent.	Santos Per Cent.	Mysore Per Cent.	Queensland Per Cent.	Columbia Per Cent.	Blue Mountain Jamaica Per Cent.
Moisture ..	3·4	3·4	3·2	3·4	3·7	3·8	2·6	2·8	2·6	3·0
Caffeine ..	1·1	1·2	1·2	1·8	1·3	1·3	1·2	1·1	1·2	1·1
Ethereal extract	14·0	15·2	14·3	10·8	14·2	14·5	13·0	15·0	13·0	11·9
Crude fibre ..	13·2	12·4	12·0	12·3	12·4	12·7	13·2	13·6	12·7	13·4
Total ash ..	4·6	4·6	4·5	4·6	4·7	4·7	4·9	4·6	4·9	5·0
Water-soluble ash ..	3·6	3·6	3·3	3·5	3·7	3·4	3·6	3·5	3·7	3·7
Alkalinity of water-soluble ash (as K_2CO_3)	2·8	2·9	2·6	2·7	2·9	2·9	3·1	3·0	3·1	3·2
Cold-water extract ..	21·2	20·8	20·8	21·4	21·7	21·1	19·6	18·2	21·0	20·5

The sp.gr. of the cold-water extract at 15·5° C. ranged from 1·0093 to 1·0105, the average being 1·0097. Whilst these coffees were very similar to ordinary coffee in chemical characteristics, some of them showed pronounced differences in aroma and flavour.

AMMONIA IN TOILET PREPARATIONS.—Ten samples used in the non-electric method of hair-waving consisted of aqueous solutions of ammonia and sodium sulphides. The ammonia-content ranged from 3·9 to 9 per cent. and six samples contained more than 5 per cent., thus coming within the scope of the Poisons Regulations. The sulphide (as hydrogen sulphide) ranged from 0·45 to 2 per cent. A solution containing 9 per cent. of ammonia would reduce hair strength to a pronounced extent, but the effect of 5 per cent. solutions would probably be transitory. In considering the question of operatives using such solutions it was calculated that if an ounce of solution (sufficient to treat the hair of two persons) containing 9 per cent. of ammonia and 2 per cent. of hydrogen sulphide were completely evaporated in a room, 12 ft. square and 12 ft. high, the concentration of ammonia in the atmosphere would be 0·007 per cent. and that of hydrogen sulphide 0·001 per cent. Such concentrations, according to authority, are non-poisonous, though objectionable in odour. The process is noxious and, if not unhealthy, certainly vitiates the air.

PARAFFIN AS "MACASSAR" OIL.—There is no evidence available that genuine macassar oil has any beneficial effect on the hair or prevents baldness. The hair oil described as "Macassar" in Queensland was found to consist almost entirely of paraffin oil. To claim that this oil is a "scalp food" suggests colossal ignorance of human metabolic processes.

LEAD IN BONE.—Fifty-six specimens of human skull and rib-bone were examined for lead by a wet oxidation process followed by extraction and estimation with dithizone. The specimens included both normal and nephritic cases. In no instance was a quantity of less than 1 mg. of lead per 100 g. of material found. The skull contained about twice the proportion found in the corresponding rib.

TRANSPORT OF "SODA CRYSTALS."—Ordinary washing soda (37 per cent. of Na_2CO_3) begins to "weep" at 90° F. and at 95° F. liquefies and causes damage to adjacent goods. These temperatures are often reached in Queensland, and the fact that more serious damage is not often reported is probably due to the chilling effect as the water of crystallisation is thrown off. Neither soda ash nor "bath salts" ("crystal carbonate") exude water in this way; they might be used as substitutes for "soda crystals."

Palestine

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1938

THE chemical work supervised by the Government Analyst (Mr. G. W. Baker, F.I.C.) is summarised in a special section of the Annual Report of the Department of Health. The number of samples examined under the Food Ordinance Rules was 8738, and 454 of these were adulterated. The principal foods examined were raw milk 4945 (137 adulterated), butter 565 (78 adulterated), semni 1547 (39 adulterated), olive and other oils 698 (114 adulterated), coffee 178 (13 adulterated).

JAM.—The Ordinance defines jam as some kind of fruit or fruits with sugar. The kinds of fruit must be stated on the label, and the addition of pectin, fruit juice and glucose is permitted. The cheaper jams are little more than pectin jelly coloured and flavoured. Of the 68 samples examined, 27 were returned as below standard.

ARTIFICIAL HONEY.—Various kinds of artificial so-called honey were examined. Some were cane or glucose syrups, whilst others were imitations of genuine honey made from invert sugar to which a honey flavour had been added. The colour tests for artificially inverted sugar did not always give positive results with these products.

APPLICATION OF BEAM'S TEST FOR HASHISH.—In one case in which a "nargileh" (hubble-bubble pipe) had been submitted it was possible to get a good result by applying Beam's test for hashish to the petroleum spirit washings from the bowl and stem of the pipe.

EXAMINATION OF BURNT CURRENCY NOTES.—In a claim for payment in connection with the charred remains of alleged currency the inscriptions on many of the notes could be identified by completing the ashing process (*cf.* Mitchell, ANALYST, 1925, **50**, 174), and after prolonged search 27 different numbers on notes were read and recorded.

ARSENICAL INSECTICIDES AND WINE.—It has been noted that the use of arsenical insecticides in the vineyards may result in contamination of the wine. In some instances such wines have been successfully treated with iron oxide.

NEUTRAL SALTS AND SOILS.—In a special investigation it was found that the observation that the *p*H of soil is lowered by the addition of a neutral salt is valid for arid soils as well as for humid. All the processes that render humid soils unsaturated take place also in arid climates, but to a less extent.

Experiments on the effect of saline water on the "loess" type soils of the Beersheba area showed that under laboratory conditions there was little accumulation of salt by evaporation, but base exchange produced alkalinity. The soil was highly calcareous and the water used was very saline, containing 300 parts of chlorine per 100,000.

New Zealand Pharmacy Act

DEFINITION OF A DRUG

THE New Zealand Pharmacy Act, 1939, came into force on January 1st. The Act, which amends the 1908 Act, gives power to the Board of the Pharmaceutical Society of New Zealand, to make rules *inter alia* to promote proper conduct among pharmacists, such as regulating, advertising and prohibiting the use of specified methods of selling drugs. Membership of the Society is compulsory for pharmacists.

In the Act "drug" means any drug (as described in any official pharmaceutical publication) used in the treatment, prevention, investigation or alleviation of any

disease, illness or injury affecting human beings. "Official pharmaceutical publication" means the latest edition for the time being of the British Pharmacopoeia or of the British Pharmaceutical Codex, and includes any supplement or addendum to either of the said publications.

The First Schedule of the Act gives a list of articles the sale of which is uncontrolled. These include acetylsalicylic acid tablets, camphorated oil, cascara, malt and oil, senna leaves, etc. Other B.P. and B.P.C. preparations may be sold only by pharmacists.

British Pharmacopoeia Commission

REPORT OF THE COMMITTEE ON GENERAL CHEMISTRY*

THIS report has been published in order to provide the opportunity for medical practitioners, pharmacists, analysts, manufacturers and others who may be interested, to criticise it and to suggest emendations before the preparation of the new Pharmacopoeia reaches its final stages.

SECTION I.

The Sub-Committee on Alkaloids and Alkaloidal Salts have reviewed the monographs submitted to them, in so far as the descriptions, characters and tests for identity and for purity are concerned. They recommend certain changes (mainly concerned with the melting-points) in nine monographs.

SECTION II.

The Sub-Committee on General Organic Chemicals recommend changes or additional requirements in 19 monographs.

AETHER.—The Sub-Committee recommend that the monograph on Anaesthetic Ether in the current Pharmacopoeia should be continued, and the quality now described as "Aether" should be named "Aether Solvens, Solvent Ether."

GLYCERINUM.—The refractive index should read "1·4696 to 1·4726" instead of "1·470 to 1·472." A new test for reducing substances is proposed.

UREA.—The synonym "Carbamide" should be inserted. The m.p. (130°–132°) should be given as a Test for Purity.

SECTION III.

The Sub-Committee on Inorganic Chemicals recommend changes or additional requirements in 42 monographs and in Appendix I.

APPENDIX VI.—For the *Quantitative Determination of Lead* the Sub-Committee recommend the adoption of the ether-extraction method, and the necessary additions to the table on pp. 553 to 558 of the B.P., 1932, are given. These include the following limits for lead in p.p.m. Acidum Mandelicum, 5; Calcii Mandelas, 5; Ferri Carbonas Saccharatus, 50; Ferri et Ammonii Citras, 50; Ferri et Quininae Citras, 50; Ferri Subchloridum Citratum, 75; Ferri Sulphas, 30; Ferri Sulphas Exsiccatus, 50; Liquor Ferri Perchloridi, 15; Magnesii Sulphas Exsiccatus, 10; Potassii Chloridum, 5; Sodii Metabisulphis, 20; Sodii Phosphas Exsiccatus, 10; Sodii Sulphas Exsiccatus, 10.

APPENDIX VII.—*Quantitative Test for Arsenic.*—Additions are required in relation to certain substances which are to be added to the Pharmacopoeia. Amounts to be taken for the test are prescribed, and the following limits (p.p.m.) for arsenic are recommended:—Acidum Mandelicum, 2; Bismuthi Subgallas, 2; Calcii Laevulas, 2; Calcii Mandelas, 2; Magnesi Sulphas Exsiccatus, 5; Potassii Chloridum, 1; Sodii Metabisulphis, 5; Sodii Phosphas Exsiccatus, 10; Sodii Sulphas Exsiccatus, 4.

APPENDIX VIII. C.—*Limit Test for Iron.*—A colorimetric method based on the use of ammonium thiocyanate is described. The comparison is made in Nessler cylinders.

APPENDIX V.—*Qualitative Reactions and Tests for Substances mentioned in the Pharmacopoeia Tests*, regarded as specific, are given for 22 metals or acid radicals. Eight additional Reagent Solutions are proposed.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Sugars in Flours. W. Iwanowski and G. Grabouska. (*Ann. des Fermentations*, 1938, p. 432; *J. Pharm. Belg.*, 1940, **22**, 24.)—The action of diastase and micro-organisms during the determination of sugars in flours can be prevented by using an alkali solution of exactly controlled concentration. The authors recommend a mixture of 75 per cent. of 0·15 *N* sodium carbonate solution, 25 per cent. of 0·15 *N* sodium bicarbonate solution and a few drops of chloroform. With this solution no decomposition of the sugars, starch or proteins occurs.

E. M. P.

Determination of Formic Acid in Foodstuffs. J. Grossfeld and R. Payfer. (*Z. Unters. Lebensm.*, 1939, **78**, 1–30.)—It is known that formic acid is not completely volatile in steam, owing to the formation of a hydrate, and the present work is concerned with its volatility in the vapour of organic solvents that are insoluble in water. It was found that no decomposition of formic acid took place when it was boiled for several hours in toluene, benzene or petroleum spirit, but only by a prolonged distillation-period or a large excess of solvent could formic acid be completely distilled with benzene or light petroleum spirit. On the other hand, a yield of over 95 per cent. was obtained from a mixture of 6 ml. of a solution of the acid in water and sufficient toluene or benzine (b.p. 100° to 110° C.) to produce distillates of 100 or 200 ml., respectively. Similar results were obtained with acetic and propionic acids in toluene, but the yields of lactic and butyric acids were less, and those of benzoic and valeric acids were still poorer; the yield of nonylic acid was only about 2·4 per cent. Prolonged distillation with toluene or benzene in presence of phosphoric acid results in the caramelisation of sugars, and the consequent production of formic acid and allied substances. The determination of formic acid by means of bromoacetic acid is unsatisfactory when the solutions are very dilute, and errors may be caused by salicylic, malonic, oxalic, lactic or tannic acid. Caramelisation of sugar is minimised if only 60 ml. of toluene or 120 ml. of benzine are used, although the yield of formic acid is then only 75 per cent.; losses may occur if the distillation is carried out too rapidly. "Interrupted distillation," in which the distillation is carried out in a special apparatus in stages, with addition of water whenever caramelisation starts, is therefore adopted (see below) as a compromise between the above limitations. In this way yields exceeding 97 per cent. can be obtained, except when the quantity of formic acid present is large. Where the quantity of formic acid is very small in relationship to the sugars present, it is desirable first to separate the former before distillation by means of a "perforation" process in a special apparatus (see below), lime water being used to fix the free acid. This, in turn, necessitates a solution that is quite free from colloidal substances, and a modification of the Carrez method of clearing is described, which does not involve the risk of the formation of ammonium formate by the hydrolysis of hydrocyanic acid. Inversion of sucrose with heat produces small quantities of formic acid detectable by the method

described, most of the reducing substances formed being left in the residue after distillation; inversion at room-temperature produces less of the interfering substances. The method finally recommended is as follows:—A solution of the sample (*e.g.* 125 g. of honey), which should not contain more than 100 mg. of formic acid, is diluted to 150 ml. in a 250-ml. graduated flask and acidified with 20 ml. of sulphuric acid (1 + 3). It is then cleared by the addition of 5 ml. of a 15 per cent.* solution of potassium ferrocyanide, followed, after shaking, by 5 ml. of 30 per cent.* zinc sulphate solution; the mixture is then made up to 250 ml., shaken, and filtered on a dry folded paper on which has been sprinkled a little kieselguhr. Clearing has been satisfactory if on shaking equal volumes of the filtrate and ether in a test-tube, no emulsion forms at the interface. If an emulsion does form, 200 ml. of the filtrate are treated with 25 ml. of a solution containing 60 g. of sodium phosphate and 100 g. of sodium tungstate per litre, and the mixture is diluted to 250 ml. and filtered on the next day through a dry folded paper; in many cases this latter stage of clarification is unnecessary. The "perforation" process then follows, 200 ml. of the filtrate being placed in the apparatus, which consists of a narrow vertical container (capacity, 400 ml.) fitted with a reflux-condenser and a side-arm just above its mid-point. Immediately under the lower end of the condenser is a narrow vertical tube, which is placed centrally in the container; this widens out slightly at the top, and at the bottom, where it rests on the base of the container, it is bent upwards and terminates in a horizontal sintered glass plate (G.1). The side-arm delivers into a conical flask which contains 0·5 g. of calcium oxide and 50 ml. of ether, and sufficient ether is added to the container to form on top of the aqueous solution a layer which just overflows into the side-arm without allowing any of the water layer to do so; all joints are of ground glass. The container is heated so that the ethereal layer in it evaporates, condensate being returned by the reflux condenser to the central tube, down which it passes and leaves as a stream of fine droplets through the sintered plate. These droplets pass up through the water layer to supplement the ethereal layer above it, and the excess of ether overflows through the side-arm. This operation lasts 5 to 6 hours, after which the distillate is evaporated and the mixture of calcium salts of organic acids and calcium hydroxide which remains is extracted for 5 minutes with 15 ml. of water, to which is added a little decolorising charcoal. The mixture is then filtered and the filtrate and washings are evaporated in presence of a little pumice powder, 5 ml. of water and sufficient 25 per cent. phosphoric acid (sp.gr. 1·154) to liberate the acids (*e.g.* 1 ml.) being added to the residue. This mixture is then distilled with 150 ml. of benzine (b.p. 80° to 90° C.) in a Payfer apparatus, the receiver of which is a wide burette-tube arranged vertically with the tap at the lower end, and joined at the top to a wider tube which is fitted with a reflux condenser. At the point where the tube widens, a side-arm (in the top end of which is inserted the outlet from a small graduated tap-funnel) leaves at a downwards angle, and terminates in a conical flask fitted with a ground-glass joint, which contains the mixture to be distilled. In this way a measured quantity of water may be added through the tap-funnel during the distillation ("interrupted distillation," see above), and the volume of benzine distilled and the distillate may be

*g. per 100 ml.

measured and easily removed from the receiver. The same conical flask used as a receiver in the "perforation" process can conveniently serve subsequently as the distillation flask. Distillation is carried out at such a rate that the distillate just falls from the condenser in a continuous stream, and when 3·5 ml. of aqueous distillate have been collected a further 5 ml. of distilled water are added to the distillation flask from the tap-funnel. When this, too, has distilled over 5 ml. more of water are added, and so on, until an aqueous distillate of at least 19·5 ml. is obtained; this takes about 45 minutes. The aqueous portion of the distillate is drawn off about 10 minutes after the conclusion of the distillation and evaporated, together with the washings from the apparatus, in presence of 1 g. of calcium carbonate. The dry residue is extracted with water, the extract is filtered, and the residue is washed until the filtrate amounts to 50 ml. The filtrate is then heated for an hour in a boiling water-bath with 15 ml. of a solution prepared by heating 10 g. of mercuric chloride, 4 g. of sodium chloride and 10 g. of crystalline sodium acetate with 100 ml. of water; for 1 hour on the water-bath it is cooled and filtered (*cf.* C. Zäch, *Mitt. Lebensm. Unters.*, 1933, **24**, 35); 15 ml. of this solution will oxidise up to 127 mg. of formic acid. After the oxidation the solution is filtered on a weighed glass crucible (No. 10G.3), and the precipitate is dried and weighed; 1 g. of Hg_2Cl_2 weighed $\equiv$ 97·2 mg. of formic acid. The benzine may be recovered for re-use by extracting it with a quarter of its volume of water, then distilling it with sodium hydroxide solution, and finally clearing it with kieselguhr and filtering. The "perforation" process is essential with honey if its sugar-content is more than 100 times its formic acid content. In presence of alcohol the sample should be shaken with calcium carbonate until neutral, and the alcohol then removed by evaporating the mixture on the water-bath to half its volume. The solution is then decolorised with activated carbon, filtered and distilled as described. Values found were as follows:—Natural blossom honeys (4 samples), 2·9 to 5·8; leaf honey, 20·9; artificial honey, 18·6; cherry juice (preserved with formic acid), 218·5 and 242·5; raspberry juice (preserved with formic acid), 293·9; currant juice, 6·6; blood-orange juice, 2·8; sweet-orange juice, 2·8; maple syrup, 30·4; "food syrup," 23·4 mg. of formic acid per 100 g. J. G.

The Bellier Test and the Blarez Test. Application to Olive and other Oils. R. Marcille. (*Ann. Chim. anal.*, 1939, **21**, 311–321.)—The technique of the Bellier test is described in detail. The following values for different oils were obtained:—arachis, 38–41; coconut, 10·5; cod-liver, 9·5; mastic tree oil, 16·75–17·75; linseed, 16·5–20; olive, 9·5–19; castor, 0·5; soya bean, 16–19; tea seed, 7–10. The following results were obtained with olive oils of different origin:—Morocco, 10·5; Tunis, 16; Tunis +10 per cent. of arachis oil, 19; Sfax, 17; Sfax +10 per cent. of arachis oil, 20·5. Very acid olive oils, oils from fermented olives and marc oils, even when refined, tend to give precipitates attributed to wax-like substances, and with such oils the tube should be left for some time at 22–25° C.

Bellier Values of Solid Fatty Acids.—The determination of the Bellier values of mixtures of solid fatty acids gives results more definite than are obtainable by titration or determination of the melting-point. Thus, mixtures of pure palmitic and stearic acids gave the following results:

Stearic acid, per cent.	0	10	20	30	40	50	60	75	100
Melting-point °C. ..	62	60·1	57·5	55·1	56·3	56·6	60·3	64·1	69·2
Bellier value ..	19·5	22	23·5	24·75	26	27	28	29·5	33·5

Similarly with mixtures of palmitic and arachidic acids:

Arachidic acid, per cent.	0	10	20	50	100
Melting-point, °C. ..	61·5	56·5	55	61	73·5
Bellier value ..	19·5	36·5	44	53	60

Special applications of the test are discussed, such as its application to the detection of the adulteration of arachis oil with linseed oil.

Examination of the Oil from Canned Fish.—Sardine oils have a Bellier value ranging from 18 to 19·5 and tunny-fish oil 19·5 to 21. It is exceptional for olive oil in boxes of sardines to show a value higher than 15·75, whilst olive oil adulterated with 10 per cent. of arachis oil has not given a value higher than 19·5.

The Blarez Value.—The temperature of crystallisation of the alcoholic solution of the potassium soaps of the fatty acids obtained by saponification of 1·5 ml. of oil with 15 ml. of alcoholic potassium hydroxide (45 g. per litre) is called the Blarez value. Pure olive oils give figures between 10 and 16 with an average of 12, and the addition of 10 per cent. of arachis oil raises the figure to 16·5; of 20 per cent. to 18·75; of 30 to 21; of 50 to 25·5, whilst the value for pure arachis oil is 28. Olive oils from canned fish may show abnormal figures and the results should be controlled by determining the Bellier values. D. G. H.

Fatty Acids and Glycerides of the Oil from Sapota Seeds. N. L. Vidyarthi and V. Mallya. (*J Indian Chem. Soc.*, 1939, **16**, 443–448.)—The evergreen sapota trees (*Achras sapota*, N.O. *Sapotaceae*), grown in southern India, produce edible fruits containing 2 or 3 seeds which are wasted. The easily removable hard shells of the seeds enclose the kernels (50 per cent. of the seed), which contain about 20 per cent. of light-coloured oil extractable with carbon tetrachloride. A sample of the oil had the following characteristics: sp.gr. at 31° C., 0·8725; n_D^{31}, 1·463; saponification value, 205·4; iodine value (Wijs), 59·8; Reichert–Meissl value, 2·8; Hehner value, 92·6; acid value, 8·94 per cent. (as oleic acid); unsaponifiable matter, 1·8 per cent. The component acids of the oil were: lauric, 1·6; myristic, 6·2; palmitic, 12·6; stearic, 12·0; oleic, 66·2; linolic, 1·4 per cent. The glycerides were calculated from data obtained by oxidising the oil with potassium permanganate in acetone, and by systematic crystallisation from acetone, and were: oleo-palmitostearin, 5; dioleomyristin, 23; dioleopalmitin, 36; dioleostearin, 28; triolein, 5; with 3 per cent. of disaturated mono-olein, in which the saturated acids are probably lauric, myristic and a little palmitic. No fully saturated glycerides were present. D. G. H.

Fatty Acids and Glycerides of the Fat from the Seeds of *Garcinia indica* (Kokum butter). N. L. Vidyarthi and C. J. Dasa Rao. (*J. Indian Chem. Soc.*, 1939, **16**, 437–442.)—The seeds from *Garcinia indica* trees (N.O. *Guttiferae*), growing on the western coast of the Madras and Bombay Presidencies, contain 20 to 25 per cent. of kokum butter, used for edible and medicinal purposes. The fat extracted from the crushed seeds with carbon tetrachloride had the

following characteristics:—sp.gr. at 40° C., 0·899; n_D^{40}, 1·4571; m.p., 39·4° C.; saponification value, 189·2; iodine value (Wijs), 36·7; free fatty acids (as oleic), 7·8 per cent.; unsaponifiable matter, 1·2 per cent. By the lead-salt separation and ester fractionation methods the fatty acids were found to consist of: myristic, 1·2; palmitic, 5·3; stearic, 52·0; oleic, 41·5 per cent. The neutral fat was oxidised in acetone and also submitted to systematic crystallisation from acetone, whereby two fractions were obtained, which were hydrogenated. The component glycerides were then calculated as: tristearin, 2·0; oleodistearin, 59; dioleostearin, 21; oleopalmitostearin, 14; oleodipalmitin, 2; palmitodiolein, 2 per cent. Compared with cocoa butter and Borneo tallow the fat contains a very small proportion of palmitic acid, but the high proportion of oleo-distearin tends to make the fat harder than those. D. G. H.

New Zealand Fish Oils. III. Composition of the Depôt Fats of the Ling (*Genypterus blacodes*). F. B. Shorland. (*Biochem. J.*, 1939, **33**, 1935–1941.)—Analyses of 7 samples of ling-liver oil taken at different periods showed no significant variation in fatty acid composition, which was in general similar to the "average" marine type with increased proportions of C_{18} unsaturated acids. The accuracy of the ester fractionation procedure was tested by various methods, all of which gave similar values for the proportion of component fatty acids. The following are typical results for the composition of the fatty acids (weight per cent.) of oils from various organs, the figures in brackets representing the degree of unsaturation:

	Saturated			Unsaturated			
	C_{14}	C_{16}	C_{18}	C_{16}	C_{18}	C_{20}	C_{22}
Liver	1·9	16·9	2·6	6·5 (2·0)	34·9 (2·5)	25·1 (5·0)	12·1 (7·6)
Viscera	0·9	18·9	2·9	6·7 (2·0)	16·9 (2·9)	36·6 (5·6)	17·1 (9·4)
Roe (phosphatide)	1·3	25·0	0·9	2·1 (2·0)	20·2 (2·7)	34·4 (7·1)	16·1 (10·0)
Roe (glyceride)	—	20·4	2·0	7·0 (2·0)	30·8 (3·1)	28·7 (7·3)	11·1 (7·3)

At least 96·5 per cent. of the unsaturated C_{18} acids consisted of octadecenoic acid together with traces of octadecatetraenoic acids; there was no indication of the presence of either linolic or linolenic acid. F. A. R.

Alkaloid-content of *Extractum Hyoscyami*. J. A. C. Van Pinxteren. (*Pharm. Weekblad*, 1939, **76**, 1629–1631.)—The 2nd Supplement of the 5th Edition of the Dutch Pharmacopoeia is criticised in respect of its specification for *Extractum Hyoscyami*. It is stated that the alkaloid-content should be 0·125 to 0·150 per cent., although the only requirement of the material from which the extract is made is that it must be of Dutch origin. The method of preparation suggests that it is assumed that the alkaloid-content of the leaves used should be approximately 0·030 per cent. Data obtained by Van der Willen (*Commentaar, Ned. Pharm.* II. 487) vary between 0·02 and 0·1 per cent., whilst those found by Goddijn

(*Pharm. Weekblad*, 1927, **81**, 118) for the leaves of *Hyoscyamus niger* were 0·040 to 0·050 per cent. Extracts prepared by the author between April, 1933, and November, 1939, had alkaloid-contents of 0·20 to 0·65 per cent. (11 extracts), and the figure specified by the German Pharmacopoeia is 0·47 to 0·55 per cent. The prescribed maximum doses of *Extractum Hyoscyami* and *Extractum Belladonnae* are 300 and 80 mg. per day, respectively, the specified alkaloid-content for the latter being 1·3 per cent. It is apparent that the prescribed alkaloid-contents and maximum doses for these two products are not in the same ratio. The addition of sugar to such preparations is permitted in order to reduce the alkaloid-content to the required figure when this is exceeded. This, however, may involve difficulties in practice, as the quantity of sugar required may be very large (*e.g.* 4 times the weight of the *Extractum*), so that it may then more correctly be described by the term "*Syrupus.*" J. G.

Detection of Novocaine and Identification of Pantocaine. F. Biedebach and H. Wiegand. (*Scient. Pharm.*, 1939, **9**; *J. Pharm. Belg.* 1939, **21**, 1025.)—Ten mg. of the substance are dissolved in 30 drops of water and treated with 1 drop of 1:10 sodium nitrite solution, then with several drops of 2·5 per cent. hydrochloric acid, and finally with 20 drops of 2 per cent. phenol solution; an orange colour is produced. With novocaine there form immediately plate-shaped golden-yellow crystals, whilst with larocaine clusters of needles form after about 10 minutes. Addition of sodium hydroxide causes a red colour. The novocaine compound decomposes at about 150° C. and that from larocaine at about 120° C. When a crystal of various anaesthetics in 1 drop of water is treated with 1 drop of 10 per cent. nitrite solution pantocaine alone gives clusters of colourless needles, probably consisting of the nitrite of the base. E. M. P.

Precipitation of Alkaloids with Cuprous Chloride. J. J. L. Zwikker and A. Kruysse. (*Pharm. Weekblad*, 1940, **77**, 18–22.)—It has been shown (ANALYST, 1934, **59**, 833) that cuprous chloride produces an insoluble precipitate with cardiazol, and the reaction has now been applied as a general test for alkaloids. The reagent is best prepared as follows:—To a solution of 200 mg. of cupric chloride in 1 ml. of water in a graduated test-tube is added a solution of 250 mg. of crystalline sodium sulphite in 5 ml. of water. A white precipitate of cuprous chloride is produced immediately, and on addition of 2 ml. of 4 *N* hydrochloric acid and sufficient water to bring the volume to 10 ml., this dissolves rapidly. Cuprous bromide (prepared by the precipitation of copper sulphate with potassium bromide and reduction with sulphur dioxide) dissolved in hydrobromic acid may also be used, but is less sensitive. As a rule one volume of the reagent should be added to 4 volumes of a solution of a salt of the alkaloid, but with the cinchona alkaloids it is necessary to reverse these proportions and to use a 5 per cent. solution of the sulphate of the alkaloid in question. Under these conditions quinidine and cinchonidine in particular, produce a precipitate which is amorphous at first, and then deposits thick yellow crystals; 4 volumes of a 1:500 solution of the former will produce with 1 volume of the reagent a turbidity which is, however, redissolved if the volume of reagent is more than doubled. After 2 hours the precipitate produced with quinine is still amorphous, whilst that from cinchonine

has disappeared. This instability, which is characteristic of these precipitates in general, is attributed to re-oxidation of the cuprous ion by the air, and it is therefore particularly marked when the reaction is carried out as a drop-test on a microscope slide. The hydrochlorides of the following alkaloids are soluble and give a negative reaction:—atropine, colchicine, coniine, cytisine, ephedrine, homatropine, morphine, nicotine, novocaine, physostigmine, pilocarpine, piperine, scopolamine, solanine, sparteine and tropine; non-alkaloids which behave similarly are acetanilide, adrenaline, antipyrine, pyramidon, tyrosine, urea and urethane. Positive reactions are obtained with the hydrochlorides of aconitine, apomorphine, berberine, brucine, cevadine, cinchonidine, cinchonine, cocaine, codeine, caffeine, cotarnine, dionine, emetine, heroine, hydrastine, quinidine, quinine, narceine, narcotine, papaverine, strychnine, thebaine, theophylline (the hydrochloride of theobromine is insoluble), veratrine and yohimbine; urotropine behaves similarly, the sensitiveness of the reaction in this instance being 1 : 500,000, although for the above alkaloids it is usually about 1 : 1000. As a rule the crystals are needle-shaped, but papaverine produces square plates, often in rosette-shaped groups (sensitiveness 1 : 2000) and similar to those formed by papaverine and mercuric chloride. Hydrastinine is exceptional in that it forms needle-shaped prisms which are strongly doubly-refracting and appear deep yellow between parallel and crossed nicols. On rotating one of the nicols, however, there is no change in the appearance of the field, and no interference colours are apparent; monochromatic (sodium) light and white light give similar results. When, however, the reagent is prepared by decanting the liquid from the precipitate of cuprous chloride while it is cooling, and dissolving the residual precipitate in 2 ml. of 4 *N* hydrochloric acid, needle-shaped crystals which behave normally when observed between crossed nicols, are obtained 5 minutes after the addition of a little solid hydrastinine hydrochloride to a drop of the reagent on a microscope slide. It is to be noted that whilst morphine does not react, codeine, dionine and heroine do, and this suggests that the presence of a phenolic hydroxy-group may influence the reactivity. Cocaine reacts, whereas tropine, atropine and scopolamine (as hydrochlorides) do not, unless the concentration is at least 2 per cent., when bundles of fine needles are slowly formed; these, however, are rapidly oxidised. The difference in behaviour between cocaine and novocaine is useful for the examination of anaesthetics, especially if oxidation of the compound formed by the former is inhibited by carrying out the reaction in a test-tube under a layer of benzene. J. G.

Determination of Iodine in Thyroid and its Preparations by Cerate Oxidimetry. W. W. Hilty and D. T. Wilson. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 637–639.)—The method of Lewis (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 199) for the determination of iodide by means of ceric sulphate and that of Smith ("*Ceric Sulphate*," Vol. I, 3rd Ed., 1935: "*Ortho-phenanthroline*," 1935, G. F. Smith Chemical Co., Columbus, Ohio), depending upon volumetric oxidation with ceric sulphate and the application of *o*-phenanthroline as indicator have been applied to the determination of iodine in thyroid preparations. When thyroid gland preparations are fused with sodium carbonate, both organic and inorganic

iodine combine with sodium to form sodium iodide. This is extracted with water, and the resulting solution is acidified with hydrochloric acid and titrated with a standard ceric sulphate solution (0·005 *N*) by which the iodide is quantitatively oxidised to iodate. In the determination and in the standardisation of the ceric sulphate solution against ferrous sulphate solution the indicator consists of a solution of 1·485 g. of *o*-phenanthroline monohydrate in 100 ml. of 0·025 *M* ferrous sulphate solution. The procedure is as follows:—Finely powdered thyroid gland (1 g.) is mixed in a nickel crucible with 15 g. and covered with 10 g. of anhydrous sodium carbonate. The crucible is heated first over a burner at dull red heat, and then for 30 minutes in a muffle furnace at a temperature not exceeding 500° C. The fused mass is extracted with warm water and filtered, and the carbonaceous residue is washed until free from soluble salts. The combined filtrate and washings are neutralised to litmus paper with conc. hydrochloric acid and acidified with 20 ml. of the acid per 100 ml. After addition of the indicator (1 drop per 150 ml.) the solution is titrated with 0·005 *N* ceric sulphate solution to a bluish-green end-point persisting for one minute. One ml. of ceric sulphate solution ≡ 0·0003178 g. of iodine. Attempts to incorporate an oxidising agent in the fusion mixture led to inconsistent results, and the use of sulphuric or nitric acid to dissolve the fused mass caused high results. The accuracy of the method was tested by determining known amounts of potassium iodide in admixture with lactose. The error varied from +0·06 to −0·22 on an iodine-content of 60 per cent. The corresponding error in the U.S.P. method of assay applied to the same material varied from +1·39 to +1·59. For the determination of iodine in thyroid tablet preparations, the amount of sample taken should correspond with at least 259·2 mg. (4 grains) of thyroid gland. For calculation it may be assumed that thyroid gland contains 0·200 per cent. of iodine. The method may be modified to make it applicable to the determination of thyroxine in thyroid gland and its preparations.

A. O. J.

Volumetric Estimation of Lac in Glazed Candies. N. M. Molnar and J. Grumer. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 673–674.)—The Federal Food, Drug and Cosmetic Act (75th Congress, S-5, Sec. 402D) allows the use of lac free from arsenic or lead as a coating on candies, but not in excess of 0·4 per cent. The proposed method for its determination depends upon the solubility of the lac acids in alkali (Weinberger and Gardner, *Ind. Eng. Chem.*, 1938, **30**, 454), and for convenience in the preparation of standard solutions sodium carbonate was chosen as the alkali. The reaction is complete when the solution contains only the sodium salts of the lac acids and sodium bicarbonate (Murty, *Ind. Eng. Chem.*, 1939, **31**, 239), and phenol red was found to be the most suitable indicator. Rogers (*"Manual of Industrial Chemistry,"* 5th Ed., p. 1103, New York, D. Van Nostrand & Co., 1931) gives 8, and Murty (*loc. cit.*) 7·7, as the equivalent value of lac in terms of sodium carbonate. Experiments with pure lac confirmed the figure 8. The glazed candy (50 g.) is covered with alcohol 3A (5 parts of methyl alcohol added to 100 parts by volume of alcohol) or 2B (0·5 part of benzene added to 100 parts by volume of alcohol). As a rule, less than 40 ml. of alcohol suffice, and the mixture is allowed to stand, with occasional stirring, for an hour. The

alcoholic solution is decanted through a filter, and the candy is re-extracted with 10 ml. of alcohol and finally washed with sufficient alcohol to provide 50 or 100 ml. of solution. An aliquot portion (20 ml.) of the filtrate is mixed with 20 ml. of water, and the mixture is kept at boiling point for at least five minutes. After the addition of 3 to 5 drops of phenol red (0·1 g. dissolved in 28·2 ml. of 0·01 *N* sodium hydroxide solution and diluted to 250 ml.), the liquid is titrated while hot with standard sodium carbonate solution containing 1 mg. of sodium carbonate in each ml. The titration is continued until the red colour matches that formed when 1 or 2 drops of the sodium carbonate solution are added to a control amount of alcohol similarly treated. The number of ml. of alkali, multiplied by 8, gives the number of mg. of lac in the aliquot portion taken. Organic acids, particularly citric acid, may be present in some candy. When their presence is suspected, or when the content of lac appears high, it is advisable to titrate an aqueous extract of the candy and deduct the result from the result of the alcoholic titration. If fatty acids are present, they are extracted by means of carbon tetrachloride and, after removal of the solvent, dissolved in alcohol and titrated with the sodium carbonate solution. Since lac is soluble in carbon tetrachloride to the extent of 6·8 per cent., the figure found requires a corresponding correction. The lac remaining in the candy is then determined by the process described. Experiments with candy to which known amounts of lac had been added showed that the method is accurate. A. O. J.

Biochemical

Determination of Magnesium in Biological Material. J. P. Nielsen. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 649–651.)—The principal objection to methods for the determination of magnesium by means of 8-hydroxyquinoline (Cruess-Callighan, *Biochem. J.*, 1935, **29**, 1081; Greenberg, Anderson and Tufts, *J. Biol. Chem.*, 1935, **111**, 561; Greenberg and Mackey, *ibid.*, 1932, **96**, 419; Abst., ANALYST, **1932**, **57**, **730**) is probably in connection with the bromination of the 8-hydroxyquinoline. Greenberg, Anderson and Tufts (*loc. cit.*) have suggested a procedure involving the use of special apparatus to prevent loss of bromine. Since magnesium quinolate can be precipitated with constant composition, any measurable reaction involving the organic part of the molecule might be used in the determination of the precipitated magnesium, and experiments showed that this can be effected by the use of ammonium hexanitrato cerate as an oxidising agent, thus eliminating the troublesome bromination necessary in the previous methods. The sample of biological material, containing from 0·05 to 3·00 mg. of magnesium (as magnesium oxide), is treated with sulphuric acid, evaporated to dryness, and ignited in a muffle furnace at 500° to 600° C. The ash is dissolved in a few ml. of 6 *N* nitric acid and evaporated to dryness (this stage may be omitted if the product does not contain tin). The residue is warmed with 1 ml. of conc. hydrochloric acid and diluted with several volumes of water, and the tin oxide and silica are removed by filtration. Traces of tin may dissolve again in the hydrochloric acid, but will be removed with the iron and aluminium later. A few drops of bromine are added, the excess bromine is removed by boiling, and

the *p*H is adjusted to about 4 with dilute sodium hydroxide solution, bromocresol green being used as indicator; the final adjustment is made with 20 per cent. sodium acetate solution. A slight excess of phosphate is necessary to precipitate iron at this *p*H value. After removal of the iron precipitate, the filtrate is treated with 1 ml. of saturated sodium oxalate solution, the *p*H is adjusted to 4·4 or 4·6 with dilute oxalic acid solution, and the liquid is boiled, cooled and allowed to stand for 2 or 3 hours. The precipitate of calcium oxalate is filtered off and washed with ammonia water (1 : 50). The filtrate is acidified to the yellow shade of the indicator with dilute hydrochloric acid, concentrated to about 10 ml. and treated with 5 ml. of 8-hydroxyquinoline reagent (1 g. of 8-hydroxyquinoline in a solution containing 89 ml. of absolute alcohol, 10 ml. of conc. ammonium hydroxide and 1 ml. of conc. hydrochloric acid). The mixture is maintained at a temperature just below its boiling-point for 15 minutes. When cold the supernatant liquid is removed by means of a sintered glass filter-stick having a thin layer of asbestos over the disc, and the beaker is washed once with 95 per cent. alcohol and six to eight times with *N* ammonia until all the alcohol has been removed. The precipitate is dissolved in 5 ml. of 2 *M* perchloric acid, and the solution is diluted to such a volume that 5 ml. contains from 0·05 to 0·10 mg. of magnesium oxide. This aliquot portion is treated with 5 ml. of 0·05 *N* cerate reagent and heated in a water-bath at 96° to 100° C. (The cerate reagent is prepared by dissolving 14·5 g. of ammonium hexanitrato cerate, $(NH_4)_2Ce(NO_3)_6$, in 500 ml. of 2 *M* perchloric acid and heating the solution in a boiling water-bath for two hours. After an interval of two days the solution is standardised against 0·02 *N* ferrous ammonium sulphate solution.) The excess of cerate reagent in the solution is titrated with standard ferrous ammonium sulphate solution, *o*-phenanthroline ferrous sulphate solution being used as indicator. One mole of magnesium corresponds with 59·7 equivalents of cerate reagent. As a representative application of the method the magnesium-content of the ash of tomatoes was determined, and the results agreed well with those found by the official method of the A.O.A.C.

A. O. J.

Determination of Small Quantities of Molybdenum in Biological Materials. D. Bertrand. (*Bull. Soc. Chim.*, 1939, **6**, 1676–1689.)—For the determination of a few γ of molybdenum in 100 g. sample of dry material the following process was found satisfactory. *Destruction of organic matter.*—Calcination is preferred to wet oxidation. G. Bertrand's two-stage process is advantageous. The sample is carbonised below 500° C., the carbonaceous mass is extracted with hot water to remove salts, the residue is ashed, and the aqueous extract is evaporated to dryness along with the ash. The residue is fused with sodium carbonate in a platinum vessel; the melt is decomposed with hydrochloric acid, and the liquid is evaporated to dryness to render silica insoluble. The residue is dissolved as far as possible in hydrochloric acid, and the silica is filtered off. (Spectroscopic tests on the silica obtained indicated freedom from molybdenum.) *Separation of molybdenum.*—It is necessary to isolate the molybdenum as far as possible from various salts, such as phosphates, present in the solution of the ash, which interfere with the final sulphide colorimetric determination of molybdenum. A cupferron-extraction method is suitable. The acid solution, obtained as described above,

is diluted so that its salt concentration is below 5 per cent.; the *p*H is adjusted to about 1·6 (change point of thymolsulphonephthalein indicator), and the solution (100 to 150 ml.) is extracted several times with 10-ml. portions of chloroform after the addition of successive portions of a freshly-prepared 10 per cent. solution of cupferron. The combined chloroform extract, which contains the molybdenum together with copper, iron and traces of tin, is evaporated to dryness. Cupferron in the residue is destroyed by heating with sulphuric and nitric acids, and the bulk of the acids used is subsequently removed by evaporation. The residue is dissolved in 5 to 6 ml. of water with the addition of 0·3 ml. of conc. hydrochloric acid. Iron and tin are precipitated by adding a little hydrogen peroxide and rendering the liquid slightly ammoniacal; the precipitate is separated by centrifuging. Re-precipitation is advised. The precipitate is rejected. The solution is evaporated to dryness, and the residue is dissolved in 3 ml. of $N/10$ hydrochloric acid. *Determination of molybdenum.*—The solution is treated with 1 ml. of 10 per cent. sodium sulphide solution and heated to 70° C., and hydrogen sulphide is passed into it for a few seconds. The precipitate (copper sulphide) is filtered off and washed with a little water. To the filtrate, diluted to 9 ml., is added 1 ml. of $N/5$ ammonium chloride solution, and the liquid is boiled for 10 to 20 seconds and cooled. The colloidal solution of molybdenum sulphide thus produced is reasonably stable, varying little in colour in 15 to 20 minutes, and thus allowing the molybdenum to be determined colorimetrically. A photo-electric colorimeter was used by the author; the sensitiveness—1 to 2γ of molybdenum in 10 ml. (0·0002 g. per litre)—was somewhat greater than could be obtained by visual comparison with standards. It was concluded that the lower limit determinable was 0·002 mg. of molybdenum in 100 g. of dry organic matter; the accuracy is estimated to be about 2 to 3 per cent. when 0·05 mg. or more of molybdenum in 100 g. is present. S. G. C.

Rôle of Sorbitol in the Carbon-Metabolism of the Kelsey Plum. I. Changes in Chemical Composition during Growth and Storage. I. Donen. (*Biochem. J.*, 1939, **33**, 1611–1620.)—In extracts of the Kelsey plum, prepared by extracting the minced fruits (250 g.) with 75 per cent. alcohol, and evaporating off the alcohol to obtain an aqueous solution (250 ml.), sorbitol was identified by the following method. A portion (5 ml.) of this solution was fermented to remove sugars and then treated with 0·5 ml. of benzaldehyde and 1 ml. of 50 per cent. sulphuric acid; dibenzal-sorbitol of m.p. 172° to 174° C. was precipitated. This derivative was also employed to estimate the amount of sorbitol present, according to the method of Martin* (*Bot. Gaz.*, 1937, **99**, 48), the accuracy of which was

* In this method 75 ml. of the extract are pipetted into a flask and 1 g. of activated charcoal is added. The flask is tightly corked and well-shaken, and the solution is immediately filtered into a dry flask. A 50-ml. aliquot portion of the filtrate is pipetted into a beaker and evaporated on a steam-bath to a thick syrup. One ml. of 50 per cent. sulphuric acid and 0·5 ml. of benzaldehyde are added, and the mixture is stirred for 5 minutes and then placed in the refrigerator for about 20 hours. To the thick yellowish paste 50 ml. of cold distilled water are added, and the paste is broken up with a stirring rod, and left in the refrigerator for a further two hours. A slight excess (1·5 g.) of anhydrous sodium carbonate is added, and finally, 1 hour later, the material is removed from the refrigerator, boiled for 1 to 2 minutes, and cooled in running water. The white, amorphous precipitate of dibenzal-sorbitol is collected on a tared Gooch crucible, washed thoroughly with water, dried for 10 to 12 hours at 100° C. and weighed. One hundred mg. of sorbitol are equivalent theoretically to 196·8 mg. of dibenzal-sorbitol. The method gives almost quantitative yields over a range of 60 to 250 mg. of sorbitol.

confirmed by tests on pure sorbitol. Reducing sugars, sucrose and fructose were determined by the method of van der Plank (*Biochem. J.*, 1936, **30**, 457). In addition the dry weight, the soluble (in both 75 per cent. alcohol and in water) solids and the acidity of the plum extracts were estimated. The complete series of analyses was carried out on samples of plums picked (usually from the same trees) at regular intervals throughout the season, and again on similar samples after varying periods of storage, in order to determine the general effect of maturity on loss of sorbitol and sugar in store. It was found that on the average the mature Kelsey plum contained 16·65 g. of dry solids per 100 g. of fresh weight, this being made up of 1·5 g. of alcohol-insoluble residue (mainly hemicelluloses and pectins), 10·48 g. of sugar, 2·82 g. of sorbitol, 0·835 g. of acid calculated as malic acid, 0·35 g. of soluble organic nitrogenous material and 0·4 g. of ash. Sorbitol appeared to be stored only during the later part of the growth cycle, and in place of hexoses, when the latter had reached a maximum concentration. Loss of respirable material from stored plums occurred at the expense of sorbitol, sugar and acid. Sorbitol was rapidly lost, but the loss of sugar depended on the initial sorbitol concentration, and at 13° C. and 25° C., mature plums of high sorbitol-content showed no significant loss of sugar. Plums of low sorbitol-content showed marked loss of sugar only when most of the sorbitol had disappeared. When plums were stored at 1° C. for 25 days and then at 7·5° C. or 20° C., they showed a 10 to 15 per cent. increase in total sugar, and a slightly greater decrease in the amount of sorbitol. F. A. R.

Vitamin A and Carotenoids in the Liver of Mammals, Birds, Reptiles and Man. H. B. Jensen and T. K. With. (*Biochem. J.*, 1939, **33**, 1771–1786.)—The amounts of vitamin A and carotenoids in the livers of 21 species of mammals, 36 species of birds, 2 species of reptiles and in 8 human specimens were estimated. The livers were saponified and extracted with ether, and the extracts were used for (*a*) the measurement (in alcoholic solution) of the absorption spectrum, (*b*) the measurement of the Carr–Price reaction by means of a Zeiss–Pulfrich photometer using three different filters, (*c*) the colorimetric estimation of carotenoids, and (*d*) micro-chromatographic analysis to determine the nature of the carotenoids present. Most of the livers gave absorption spectra typical of vitamin A. It was found that the relation between the extinction value of the solution obtained in the Carr–Price reaction using filter S61, and $E^{1\%}_{1\,cm.}$ (328$m\mu$) had a fairly constant value of 2·60 to 2·75. Considerable variation was encountered in the amounts of vitamin A and carotene present in the livers even of closely related species or of species that exist on similar kinds of food. There appeared to be no simple relationship between the amount of vitamin A and carotene in the food ingested and their concentrations in the liver. Carotene was found to be present in considerable amounts in the livers of certain beasts of prey (*e.g.* foxes) and birds as well as in herbivora, but most of the livers examined were practically free from carotenoids. F. A. R.

Thiochrome Test for Aneurin in Urine as an Index of Nutritional Level. G. M. Hills. (*Biochem. J.*, 1939, **33**, 1966–1979.)—The samples of urine were preserved at an acid *p*H, 0·5 ml. of conc. hydrochloric acid or glacial acetic

acid being added; toluene was added as well to prevent mould growth. After filtration, to remove any deposit, the urine was diluted so that the amount excreted per hour was made up to 500 ml. The *p*H was then adjusted to 3–5, and two 75-ml. portions of the urine were each stirred mechanically in a centrifuge tube for 1 to 2 minutes with 25 ± 2 mg. of "Clarit" acid clay. Other aliquot portions (usually two) were similarly treated after the addition of different amounts of aneurin (less than 4γ). The adsorbates were collected by centrifuging for 2 to 5 minutes, and the supernatant liquors were discarded. The wet adsorbates were treated in the same tubes with 2 ml. of pure methyl alcohol. To provide a blank, 1 ml. of water was added to one of the tubes not containing added aneurin. The contents of the four tubes were then stirred with a stream of nitrogen, and 1 ml. of 7·5 *N* sodium hydroxide solution, followed by 1 ml. of 1·25 per cent. potassium ferricyanide solution, was added to each of the tubes except the blank. Isobutyl alcohol (12·5 ml.) saturated with water was then added to all four tubes, and the contents were stirred for 1 to 2 minutes. After standing for a few minutes the upper layer was decanted through a dry 8·5-cm. filter-paper (previously purified by exhaustive extraction with wet isobutyl alcohol) into a test-tube specially selected for fluorescence measurement and calibrated at 10 ml. When 10 ml. of the solution had been collected, the tube was stoppered and the fluorescence was measured in an improved type of Cohen fluorometer. The fluorescence (expressed as a percentage of that produced under similar conditions from 1γ of aneurin, oxidised in pure solution with 0·3 ml. of 1·25 per cent. potassium ferricyanide solution) was plotted against the amount of added aneurin, and the curve so obtained was produced backwards until it cut the abscissa drawn at a level corresponding to the fluorescence of the unoxidised blank. The length of the intercept so produced gave the aneurin-content of the sample. The most important modification introduced into the fluorometer consisted in the use of a blue colour-filter (Wratten 49A or 48 with Weston "Photronic" cells types I or II, respectively) to bring the maximum response of the cell to a wave-length of 460 to 470$m\mu$, corresponding with the maximum fluorescence of thiochrome.

F. A. R.

Distribution of Aneurin in Foods determined by Chemical Analysis. M. Pyke. (*J. Soc. Chem. Ind.*, 1939, **58**, 338–340.)—The thiochrome method of assaying aneurin has been applied to foodstuffs, with results that agree well (with certain exceptions) with the values obtained by the rat bradycardia method. A novel method of extracting the vitamin has been used. To 20 g. of the finely-minced or powdered foodstuff is added a solution of 0·1 per cent. of pepsin in 0·33 per cent. hydrochloric acid, and the volume is made up to 97·4 ml. The mixture is incubated overnight at 37° C., 2·6 ml. of *N* sodium hydroxide solution and 100 mg. of takadiastase are added, and incubation is continued for a further 5 hours. In this way the aneurin released from the tissues of the foodstuff and its pyrophosphate is hydrolysed to the free vitamin. A part of the solution is centrifuged (not filtered) and two 3-ml. portions are pipetted into graduated cylinders containing the following reagents kept stirred by means of a stream of nitrogen. The first cylinder contains 2 ml. of methyl alcohol, 1 ml. of 30 per cent. sodium hydroxide

solution and 1 ml. of 1 per cent. potassium ferricyanide solution. The second cylinder contains 2 ml. of methyl alcohol and 1 ml. of sodium hydroxide solution only. After 1 minute the solutions are made up to 10 ml. with water, 13 ml. of isobutyl alcohol are added, and the solutions are well mixed. Ten ml. of the supernatant layer in each tube are pipetted into uniform test-tubes, and 1 ml. of alcohol is added to each. A standard solution of thiochrome (in isobutyl alcohol) is added, 0·1 ml. at a time, to the aliquot portion prepared without ferricyanide, until the intensities of fluorescence match when the two tubes are held side by side at an angle of 45° against a nickel oxide filter arranged in a vertical position to transmit the ultra-violet light of a mercury vapour lamp. The standard solution of thiochrome is prepared by treating a solution containing a known amount of aneurin in the same way as in the test. The following represents some of the more important results obtained, values being expressed in I.U. per 100 g.—apples (different varieties) 6 to 23; apricot, fresh 23, dried 57; bacon, raw 88; banana 8; beans, tinned-baked 17; raw butter 140; beef 23; biscuits 0 to 19; bread, wholemeal 50, proprietary brown 50 to 95, white 13; cabbage 23; carrot, raw 15; cauliflower 49; cheese (18 different kinds) 0 to 21; chocolate 10; cod's roe, smoked 300; egg 86; hake 13; halibut 38; ham, cooked 190; herring 2; herring roe (hard) 10; honey 6; jam (apricot, blackcurrant, raspberry, strawberry) 0, (greengage, plum) 25; kidney, ox 57, sheep 76; lentils 170; lettuce 23; liver, calf 66, ox 61; milk, fresh 10, condensed sweetened 32, dried skimmed 85; mutton 34; oatmeal, breakfast 95; peanut 228; peas (green) 120; plaice 65; pork 475; potatoes, boiled or fried 40; salmon, tinned 38; sugar 2; tomato 15; veal 57. F. A. R.

Estimation of Vitamin B_1 in Cerebro-spinal Fluid. H. M. Sinclair. (*Biochem. J.*, 1939, **33**, 1816–1821.)—The method previously described (*cf.* ANALYST, 1939, **64**, 214) has been applied to cerebro-spinal fluid. From 1 to 4 ml. of the latter are added to flasks containing the medium (with 0·4 per cent. of asparagine), the flasks are sterilised by tyndallisation and inoculated with *Phycomyces blakesleeanus*. The weight of the fungus produced after 10 days is proportional to the amount of aneurin present. The presence of the vitamin is confirmed by the fact that no growth is obtained when the vitamin is converted into thiochrome by alkaline potassium ferricyanide solution. Cerebrospinal fluid, like blood, contains an adjuvant factor, but in much smaller amounts. Consequently the values obtained for the aneurin-content are higher than the true value, but a correction can be applied for this source of error by multiplying the weight of fungus obtained with 1 ml. of c.s.f. (or blood) by the factor:

$$\frac{\text{weight obtained with excess vitamin}}{\text{weight obtained with 1 ml. of c.s.f. (or blood) in presence of excess vitamin}}$$

The method estimates aneurin both in the free state and combined as cocarboxylase; normal c.s.f. contains none of the latter. The method was applied to 272 samples of c.s.f. obtained from hospital patients, but apart from the fact that pathological samples tended to give higher values than normal samples, the method appears to be of no clinical value. F. A. R.

Estimation of Aneurin in Blood. II. Further Modification of Meiklejohn's Method. H. M. Sinclair. (*Biochem. J.*, 1939, **33**, 2027–2036.)—The method of assaying aneurin by measuring the growth-rate of *Phycomyces blakesleeanus* (*cf.* ANALYST, **1939**, **64**, 214, and preceding abstract) does not give satisfactory results for blood, since factors are present in blood that have an adjuvant action. Thus samples of 1, 2 and 3 ml. of blood do not usually give the same values per unit volume. The same values can, however, be obtained by multiplying the weight of fungus obtained in the presence of blood by the factor:

$$\frac{\text{weight of fungus obtained with excess aneurin}}{\text{weight of fungus obtained with excess aneurin and blood}}$$

Four 2-ml. samples of the blood, two without and two with added excess aneurin ($2{\cdot}5\gamma$), are incubated with the organism as previously described, and the mycelia are filtered off, dried and weighed. The amount of growth produced by a solution of $2{\cdot}5\gamma$ of aneurin is ascertained in a similar way. The weight produced by the blood with the excess aneurin is then multiplied by the factor given above and the corrected value is converted into amounts of aneurin from the growth-vitamin curve obtained with the pure substance. F. A. R.

Quantitative Estimation of Nicotinic Acid in Urine. E. Bandier. (*Biochem. J.*, 1939, **33**, 1787–1793.)—The colour reaction previously described (Bandier and Hald, *cf.* ANALYST, **1939**, **64**, 441) has been applied to the estimation of nicotinic acid in urine. Five ml. of urine and 2 g. of sodium chloride are thoroughly mixed in a 50-ml. graduated flask fitted with a glass stopper, and 45 ml. of acetone are added from a burette. The mixture is shaken to extract the nicotinic acid and then centrifuged. Twenty ml. of the acetone extract (equivalent to 2 ml. of urine) are pipetted off and transferred to a flask, together with 3 ml. of water. The acetone is evaporated, and the residual solution is transferred quantitatively to a 20-ml. graduated flask with the aid of 5 ml. of 2 per cent. potassium dihydrogen phosphate solution. The flask is heated for 5 minutes on a water-bath at 75° to 80° C., 1 ml. of a freshly-prepared 4 per cent. solution of cyanogen-bromide is introduced, and, after 5 minutes' further heating, the flask is cooled. Ten ml. of a freshly-prepared saturated solution (5 per cent.) of metol are added, and the solution is diluted to 20 ml. After standing for 1 hour at room temperature with protection from the light, the colour of the solution is measured in a Pulfrich photometer (filter S43) against a solution containing the same amounts of reagents made up to 20 ml. with distilled water. The blank is prepared by treating a second 20-ml. portion of the acetone extract as described above and adding to it 0·18 ml. of 2 *N* sulphuric acid instead of metol. The colour is measured in the Pulfrich photometer (filter S43) with distilled water in the other cell. The value found, corrected, of course, for the thickness of the cell, is subtracted from the first reading, the nicotinic acid content being calculated from the difference by comparison with readings obtained with a standard solution. In some instances the blank value may amount to 6 times the value of the colour reaction proper.

The reaction is given, not only by nicotinic acid, but also by nicotinamide (free and combined as co-enzyme), nicotinuric acid and nicotine, the relative

colours produced by equimolar concentrations of these 4 substances being, respectively, 100, 142, 42, 8. Trigonelline and methylpyridinium hydroxide do not react. The above-mentioned derivatives of nicotinic acid are converted into the acid itself by alkaline hydrolysis, a procedure that enables a fairly accurate estimation of the total (free and combined) nicotinic acid to be made. Fifteen ml. of urine and 2 ml. of 10 *N* sodium hydroxide solution are mixed in a 20 ml. graduated flask which is closed with non-absorbent cotton wool and then heated for 30 minutes on a boiling water-bath. After cooling, the *p*H of the solution is adjusted to 5 by the addition of conc. hydrochloric acid (about 1·6 ml.), and the volume is made up to 20 ml. After centrifuging, the analysis is continued as described above.

The amount of nicotinic acid found after hydrolysis was 2 to 3 times that found prior to hydrolysis. Recoveries ranging from 96 to 103 per cent. (10 experiments) of added nicotinic acid were obtained. After the oral ingestion of 90 mg. of nicotinic acid, 14 per cent. thereof was found to have been excreted, chiefly during the first hour. Some of this was in the form of nicotinuric acid or a closely related substance. F. A. R.

Estimation of Nicotinic Acid in Urine. L. J. Harris and W. D. Raymond. (*Biochem. J.*, 1939, **33**, 2037–2051.)—A careful study of König's reaction was made, and as a result *p*-aminoacetophenone was selected for use in the test in preference to other aromatic amines. Furthermore, since the coloured substances formed in the reaction were found to be sensitive to light and to changes in *p*H, modifications were introduced to overcome the discrepancies arising from these causes. To a 25-ml. specimen of the urine, 5 ml. of 20 per cent. sodium hydroxide solution are added and the mixture is heated for 30 min. on a steam bath to convert any nicotinamide into free nicotinic acid. The solution is then treated with 2 ml. of 4 per cent. sodium bicarbonate solution (to help stabilise the end-point) and neutralised accurately to *p*H 6 by the cautious addition of conc. hydrochloric acid from a micro-burette (bromothymol blue as external indicator). The contents of the flask are transferred to a 50-ml. graduated flask and made up to the mark. Four 10-ml. portions of the prepared urine are transferred to four 15-ml. standard flasks, into two of which 0·2 ml. and 0·4 ml. of a standard solution of nicotinic acid (100γ per ml.) have previously been introduced. All the flasks are then immersed for about 10 min. in a bath kept at 80° C. and shaded from the light. Two ml. of freshly-prepared cyanogen bromide solution (a 10 per cent. solution of potassium cyanide is added, drop by drop, to a saturated solution of bromine until decolorised) are added to each of the flasks except one of those not containing added nicotinic acid, which is to serve as blank. After being rotated to mix the solutions, the flasks are allowed to remain for a further 4 minutes at 80° C., and are then immersed in a bath of cold water for 4 minutes. To each is then added 0·2 ml. of amine solution (made by dissolving 5 g. of *p*-aminoacetophenone in 14 ml. of 10 per cent. hydrochloric acid and diluting to 50 ml.), the contents of the flasks are mixed, and the flasks are placed in the dark for 15 minutes. To each is then added 0·4 ml. of 10 per cent. hydrochloric acid and, after standing for a further 15 minutes in the dark, the solutions are introduced in succession into the 3-cm. cell of a Pulfrich photometer and the colours measured

with filter S47. The extinction values thus obtained are plotted against the amount of nicotinic acid added, and the resulting graph (which should be a straight line) is produced backwards until it cuts the abscissa. The distance of the point of intersection from the origin indicates the amount of nicotinic acid in the sample. Good agreements have been obtained in duplicate experiments, with an experimental error within ±10 per cent., whilst added nicotinic acid or nicotinamide is quantitatively recovered. F. A. R.

Oxalate Formation in Ascorbic Acid Solutions. A. E. Jurist and W. G. Christiansen. (*Amer. J. Pharm.*, 1939, **111**, 347–350.)—Aqueous solutions of ascorbic acid are unstable and progressively deteriorate in strength, while oxalic acid is formed as one of the products of auto-oxidation (Ghosh and Rakshit, *Biochem. Z.*, 1938, **299**, 394). The results here described show that oxalic acid is invariably present in solution, the amounts in the samples examined ranging from 0·19 to 11·14 mg. per ml. The amount of oxalic formed is not proportional to the loss of ascorbic acid on ageing. Oxalate was formed in solutions of monoethanolamine ascorbate as well as in those of the sodium and calcium salts. For the determination of the oxalic acid 10 ml. of the solution at *p*H 5·0 to 7·5 were treated with 2 ml. of 10 per cent. calcium acetate solution in a 15-ml. centrifuge tube, which was then stoppered and left for 5 days. The precipitate was separated and washed with the aid of centrifuging and finally collected on asbestos in a Gooch crucible; as little water as possible was used throughout. Finally the asbestos mat and precipitate were transferred, with 25 ml. of water, to a 150-ml. beaker containing 25 ml. of 20 per cent. sulphuric acid, the mixture was heated to 70° C., and the oxalic acid was titrated with $N/100$ potassium permanganate solution.

Evaluation of the Activity of Powders of *Veratrum viride* by the *Daphnia* Method. I. Cohen. (*Amer. J. Pharm.*, 1939, **111**, 426–429.)—When an extract (50 ml.) of *Veratrum viride*, prepared by vigorously shaking 1 g. of the powder with 100 ml. of water (or culture medium) and then filtering, is added to 50 ml. of culture medium (Bovung) containing 50 standardised 10-day old *Daphniae magnae*, a change in the behaviour of the organisms is observed. At first, the swimming activity is accelerated and also inco-ordinated, but later the *Daphniae* become exhausted and begin to settle to the bottom of the jar ("debility shift"), where they ultimately lie quiescent. The activity of the *Veratrum* extract can be estimated by noting at intervals how many of the *Daphniae* are swimming above the midmark of the jar and how many lie below it. The jars recommended for this purpose are narrow museum jars 15 × 10 × 2 cm. When appreciable differences are found in the relative activities of two extracts, a more exact comparison can be obtained by diluting the stronger of the two until the behaviour of the *Daphniae* towards both solutions is the same. The results obtained were in agreement with those obtained by assays on rats, rabbits and guinea-pigs. F. A. R.

Agricultural

Determination of Deguelin in Derris and Cubé. L. D. Goodhue and H. L. Haller. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 640–642.)—The chloroform extract of derris or cubé is easily divided into three fractions. Rotenone can be

removed by crystallisation from carbon tetrachloride (Jones, *J. Amer. Chem. Soc.*, 1931, **53**, 2738; Jones and Graham, *J. Assoc. Off. Agr. Chem.*, 1938, **21**, 148), and the remaining resin can be divided into alkali-soluble and alkali-insoluble portions (Haller and La Forge, *J. Amer. Chem. Soc.*, 1934, **56**, 2415). The last part consists largely of optically active deguelin, since racemic deguelin is obtained by further treatment of this fraction with dilute alkali. Fifty g. of finely ground material containing deguelin were extracted with chloroform in a Soxhlet extractor for 7 hours. After removal of most of the solvent the extract was dissolved in 75 ml. of ether and the solution was extracted with two 15-ml. portions of 5 per cent. potassium hydroxide solution saturated with sodium chloride. The alkaline liquids were extracted with ether which was added to the first ethereal solution and washed once with dilute hydrochloric acid (1 : 10). The alkali-soluble portion was discarded. After removal of the ether, the resin was dissolved in 40 ml. of carbon tetrachloride and the solution, seeded with rotenone carbon tetrachloride solvate, was allowed to crystallise overnight at 0° C. The solvate was then filtered off and washed with ice-cold carbon tetrachloride. The filtrate and washings were evaporated to remove the solvent, the residue was dissolved in 10 to 15 ml. of methanol and placed while warm in a 25-ml. flask with 10 drops of 40 per cent. potassium hydroxide solution. After thorough mixing of the liquids, the flask was filled with warm methanol and closed by means of a cork carrying a funnel made from a drawn-out test-tube in such a manner that no air bubbles remained in the flask and some of the liquid was forced up into the funnel. More methanol was placed in the funnel to counteract contraction on cooling and as a reserve for evaporation, and the solution was maintained at 45° C. for an hour to prevent separation of the resin before it was racemised. Racemisation was not usually complete until the liquid had stood overnight. The racemised deguelin was cooled at 0° C. for an hour. The crystals were separated by filtration without washing, dissolved in chloroform and the chloroform removed by evaporation twice with carbon tetrachloride. Finally, the deguelin was crystallised from 5 or 10 ml. of carbon tetrachloride according to the amount present. The crystals were collected on a tared Gooch crucible, washed with cold carbon tetrachloride saturated with deguelin, dried at room temperature and weighed as the 1:1 deguelin-carbon tetrachloride solvate. The amount of deguelin in the impure solvate was determined by the red colour test (Goodhue, *J. Assoc. Off. Agr. Chem.*, 1936, **19**, 118; Abst., ANALYST, 1936, **61**, 486). It was assumed that deguelin alone was responsible for the colour, and the fact that racemic deguelin gives only 80 per cent. of the colour of rotenone was taken into account when rotenone was used as the standard. Experiments showed that the solubility of deguelin in carbon tetrachloride may be compensated for by adding 0·08 per cent. when 5 ml. of carbon tetrachloride are used and 0·11 per cent. when 10 ml. are used. The amount of deguelin in the samples of derris examined varied from 0·24 to 3·9 per cent. and in the samples of cubé from 0·25 to 2·3 per cent. The high toxicity to insects of the non-crystalline portion of derris and cubé extracts, coupled with a low deguelin content, suggests the presence of unidentified compounds that contribute to the toxicity. A. O. J.

Organic

Iodimetric Determination of Organic Acids. B. Singh and S. Singh. (*J. Indian Chem. Soc.*, 1939, **16**, 343–345.)—Oxalic, tartaric, citric, malic, and glycollic acids can be determined by treatment with an excess of potassium iodide and potassium iodate in presence of a barium, zinc or magnesium salt, followed by potentiometric titration of the liberated iodine against sodium thiosulphate solution. The authors carried out the titration at 10° C., using a platinum electrode coupled with a saturated calomel electrode, and keeping the solution stirred with a mechanical stirrer. A sharp fall in E.M.F. occurs at the equivalence point. E. M. P.

Arylation of Oils and Fats. Synthesis of Tolyl Stearic Acid and its Esters. W. Kimura and J. Tsurugi. (*J. Soc. Chem. Ind. Japan*, 1939, **42**, 390–391B.)—Camellia oil (Wijs iodine value, 82·70; acid value, 2·51; ester value, 184·43; saponification value, 186·94) was used as the source of oleic acid (*cf.* Kimura, *J. Soc. Chem. Ind., Japan*, 1929, **32**, 459). The optimum conditions for arylation were found to be the presence of a 30 per cent. excess of aluminium chloride, a 1400 per cent. excess of toluene, a reaction-temperature of 25° to 34° C., and a reaction-time of 2 to 3 hours. On fractional distillation *in vacuo* of the resulting methyl esters of the tolylated fatty acids of camellia oil, the unsaturated or unchanged (*i.e.* non-arylated) constituents were obtained as a fraction of low b.p., the reaction-products of high mol. wt. as a fraction of high b.p., or in the residue, and the tolyl stearic acid methyl ester as a pale yellow oil, with b.p. 232° to 245° C. (3 mm.), n_D^{30}, 1·4754 to 1·4781 and sp.gr. (30° C.), 0·9153 to 0·9167. The tolyl stearic acid separated from the ester was a pale yellow viscous oil, the yield of which was lowered by the side-reactions. Constants of the tolylated camellia oil were as follows:—Wijs iodine value, 9·92; acid value, 7·36; ester value, 152·8; saponification value, 160·16; n_D^{30}, 1·4700. This reaction may also be used as a means of separating the saturated and unsaturated constituents of oils and fats, the fatty acid component being any mono-ethylenic acid or halogen fatty acid (or a derivative of these), while the aromatic constituent can be benzene or its homologues or their derivatives (*cf.* Nicolet and De Milt, *J. Amer. Chem. Soc.*, 1927, **49**, 1106). J. G.

Occurrence of an Isomer of Ricinoleic Acid in the Fatty Oil from the Seeds of *Vernonia anthelmintica*. N. L. Vidyarthi and M. V. Mallya. (*J. Indian Chem. Soc.*, 1929, **16**, 479–480.)—The fatty oil obtained from the seeds of *Vernonia anthelmintica* (N.O. *Compositeae*) has been found to have an optical rotation of $[\alpha]_D^{28°}$, −10·7 and an acetyl value of 135·1. These values are not entirely due to the high percentage of unsaponifiable matter, since the mixed fatty acids freed from unsaponifiable matter had an optical rotation of $[\alpha_D^{25}]$, −7·2 and an acetyl value of 118·2 and contain about 60 per cent. by weight of a hydroxy straight-chain acid belonging to the monohydroxyoctadecenoic (ricinoleic) series. The acid is viscous and sparingly soluble in petroleum spirit, and has a saponification equivalent of 299·0 (calc. for $C_{18}H_{34}O_3$, 298·2). It differs from ricinoleic acid in being *l*-rotatory, $[\alpha]_D^{28°}$, −7·8, and the OH group appears to be in a different

position, for it is readily substituted by halogens even during the period of iodine value determination by the Wijs and Hanus methods, but on acetylation and protection of the OH group no more substitution occurs, and the exact quantity of iodine for the ethylene linkage is absorbed. The iodine value of the acid is 108·4 and that of the acetylated acid 73·8. It does not yield a solid dibromide like that reported for quince oil acid. D. G. H.

Bamboo Leaf Wax. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1939, **42**, 396B.)—About 1 per cent. of wax was extracted with hot petroleum spirit from the leaves of the bamboo *Sasa paniculata Makino et Shibata*, which grows abundantly in the mountainous districts of Central Japan. When purified by solution in ethyl acetate and treatment with animal charcoal it was a brownish-yellow, hard, brittle solid, having the following properties:—sp.gr. (25°/4° C.), 0·961; m.p., 79° to 80° C.; acid value, 14·5; saponification value, 43·4; iodine value (Wijs), 7·8; unsaponifiable matter, approximately 65 per cent. (a brownish-yellow solid; m.p., approximately 87° to 88° C.; iodine value, 12·7; acetyl value, 58·9; no appreciable quantity of sterols present). The fatty acids were hard and brownish-yellow in colour; m.p., 81° to 82° C.; neutralisation value, 121·8; iodine value, 4·7. The wax contained melissic acid ($C_{30}H_{60}O_2$), melissyl (myricyl) alcohol ($C_{30}H_{62}O$) and possibly saturated acids such as montanic acid ($C_{28}H_{56}O_2$) and cerotic acid ($C_{26}H_{52}O_2$). Compounds containing oxygen, which were either unsaponifiable or saponifiable with difficulty, were present in relatively large proportions. The wax could probably be used as a substitute for carnauba wax. J. G.

Inorganic

Non-precipitation of Cobalt and Palladium by Nitro-β-Naphthol. C. Mahr and W. Prodinger. (*Z. anal. Chem.*, 1939, **117**, 334.)—Methods for the gravimetric determination of cobalt and palladium by means of nitro-β-naphthol have been published by Mahr (ANALYST, 1934, **59**, 846). It has now been found that the reagent employed in the earlier work contained large proportions of nitroso-β-naphthol, to which the precipitation of the metals was undoubtedly due; pure α-nitro-β-naphthol, prepared from β-naphthylamine, does not precipitate cobalt or palladium solutions, and therefore cannot be used for the determination of these metals. W. R. S.

Colorimetric Determination of Iron in Aluminium and Alumina. L. Roelen. (*Z. anal. Chem.*, 1939, **117**, 385–389.)—The method utilises the bluish-green colour of alkaline colloidal solutions of ferrous sulphide, which conforms to Lambert and Beer's law. It is immaterial whether the iron is present as ferric or ferrous salt; its concentration should be 0·005 to 0·3 mg. per 100 ml. A colorimetric scale is prepared by pipetting 1, 2, 3 to 10 ml. of a standard solution (0·04 mg. of Fe_2O_3 per ml.) into 100-ml. flasks, and adding 5 ml. of 5 per cent. sodium tartrate solution and 2 *N* sodium hydroxide solution, drop by drop, to alkaline reaction. The solution is treated with 5 ml. of 10 per cent. sodium sulphide solution; the three reagents should be freshly prepared each day. After standing for 15 minutes the solutions are diluted to 100 ml.; the colour is stable for

several hours. A Pulfrich photometer is recommended in place of the scale of standards, the colour being measured against water and light filters Hg436 or S61. *Refined aluminium* (free from lead and copper).—The sawings (1 to 2 g.) are dissolved as usual in a mixture of *aqua regia* and sulphuric acid, and the solution is heated until white fumes are evolved. Silica is filtered off, and the filtrate is diluted according to the iron-content (100 to 500 ml.). A suitable amount is treated as described above. *Alumina.*—Two g. are fused with 40 g. of potassium bisulphate in a corundum crucible (a vitreosil crucible appears more suitable—ABSTRACTOR). The cold melt is dissolved in 300 ml. of water and 50 ml. of sulphuric acid (1:1), the solution is diluted to 500 ml., and 2 to 25 ml. are submitted to the test after 30 minutes' standing; the standard should contain the same amount of bisulphate. *Hydrated alumina.*—One g. is dissolved in 10 ml. of sulphuric acid (1:1) in a 100-ml. flask, and 25 ml. are taken for the test, sufficient sodium hydroxide being added to re-dissolve the precipitated alumina. *Aluminate liquor* (2 to 5 ml.) is treated with 5 ml. of sodium tartrate solution, sulphuric acid (1:5) until the aluminium hydroxide just re-dissolves, and a slight excess of 2 *N* sodium hydroxide solution. The alkaline liquid is treated with sodium sulphide, and the tint is matched after 15 minutes. W. R. S.

Determination of Aluminium in Presence of Iron and Phosphoric Acid. G. Balanescu and M. D. Motzoc. (*Z. anal. Chem.*, 1939, **118**, 18–26.)—In the analysis of soil extracts, the basic acetate precipitate is dissolved in hydrochloric acid and the solution is made up to a definite volume. In one aliquot portion the iron is determined volumetrically. Another portion is used for the determination of phosphoric acid. To the third portion sufficient sodium phosphate is added to produce a solution in which the ratio g.Fe : g.$P_2O_5 = 2$. The liquid is then treated, drop by drop, with strong sodium hydroxide solution until the iron is completely precipitated, then with 5 ml. of *N* sodium hydroxide solution, and slowly heated to boiling. The precipitate is collected and well washed with boiling water containing 5 ml. of *N* sodium hydroxide solution per 100 ml. The filtrate is cooled and neutralised with 3 *N* hydrochloric acid to phenolphthalein; the precipitate is re-dissolved by dropwise addition of *N* sodium hydroxide solution, which restores the pink colour of the indicator. The opalescent solution (80 ml.) is cleared by boiling, cooled to 50° C., treated with a 3 per cent. alcoholic solution of 8-hydroxyquinoline, and heated to boiling. The precipitate is collected in a Jena glass filtering-crucible, G4, washed with boiling water until the washings are colourless, dissolved in 3 *N* hydrochloric acid, and titrated with 0·1 *N* bromate solution (1 ml. ≡ 0·000225 g. Al). The adjustment of the Fe:P_2O_5 ratio is stated to ensure the quantitative separation of iron from aluminium by a single precipitation with sodium hydroxide. W. R. S.

Gravimetric Determination of Antimony by Means of 8-Hydroxyquinoline. T. I. Pirtea. (*Z. anal. Chem.*, 1939, **118**, 26–30.)—The acid trichloride solution is treated with an excess of reagent (7 to 8 g. of the base dissolved in a minimum of acetic acid and treated with dilute ammonia till cloudy, the cloudiness being removed with a few drops of acetic acid). The liquid is heated to 70° C., and 10 per cent. ammonia is added from a pipette, a yellow precipitate beginning

to form at *p*H 1·5. The addition of ammonia is continued until the precipitation is quantitative and the solution becomes deep yellow. The precipitate is set aside in the cold for 1 to 2 hours, collected in a Jena glass crucible (1G3 or 1G4), washed with a solution containing 0·3 g. of the base and a few drops of acetic acid per litre, dried for an hour at 105° to 110° C., and weighed. In testing for constancy of weight, the precipitate should not be heated for more than 30 minutes at a time, as it gradually undergoes a slight loss in weight. Sb factor for $(C_9H_6ON)_3Sb$: 0·2197. Antimony may be precipitated from tartrate solution by the same method, but the precipitate is of a lighter yellow colour, and has the composition

$$(C_9H_7ON)_2.C_9H_6ONSbO,$$

with an antimony factor 0·2129. The antimony determination in tartar emetic can be effected in hydrochloric or tartaric acid solution; the last-mentioned basic compound is precipitated. W. R. S.

Volumetric Determination of Chlorate and Bromate. C. Mahr and H. Ohle. (*Z. anal. Chem.*, 1939, **117**, 389–391.)—The oxidation of thiourea (ANALYST, 1939, **64**, 622) can be applied to this determination, the procedure having the advantage over reduction with ferrous salt that the reducing agent is stable and not affected by atmospheric oxygen. The excess of thiourea can be determined by means of permanganate in presence of iodide. *Chlorate.*—The chlorate solution is added to a mixture of 20 ml. of sulphuric acid (1:1), 5 ml. of 1 per cent. potassium iodide solution, and a measured excess of 0·1 *N* thiourea solution during agitation, and the liquid is heated on the water-bath to 70° C. for 10 to 15 minutes. After cooling to 35° C. it is treated with a little starch solution, diluted to 80 ml., titrated with 0·1 *N* permanganate to the appearance of a faint blue tint, diluted to 250 to 300 ml. with water (35° C.), and again titrated until a light blue end-point is reached. *Bromate.*—The bromate solution is added, drop by drop, during vigorous stirring, to the mixture described above. The excess of thiourea can be titrated at once with permanganate after addition of starch solution, dilution to 80 ml., and warming to 35° C. W. R. S.

Determination of Fluorine and Silica in the Hot-Springs of Gastein. R. Bisanz and F. Kroupa. (*Chem.-Ztg.*, 1939, **63**, 689–691.)—Samples from six different springs contained 1·77 to 3·40 mg. of fluorine and 35·5 to 45·4 mg. of silica per kg. of water. Fluorine was determined by titration with thorium nitrate with the use of sodium alizarinesulphonate as indicator (Armstrong, *J. Amer. Chem. Soc.*, 1933, **55**, 1741) and also gravimetrically as calcium fluoride, the results of the two methods showing good agreement. Silica was determined (*a*) by direct separation through evaporation with hydrochloric acid; (*b*) by precipitation with zinc oxide and ammonium carbonate; in either method the nett weight of silica was obtained by volatilisation with hydrofluoric acid. The values were reasonably concordant, but, despite the possibility of slight loss of silica as fluoride in method (*a*), slightly higher results were obtained than with method (*b*). This point is to be further studied. S. G. C.

Determination of Fluorine in Wood [Treated with Fluoride Preservative]. B. Ikert. (*Chem.-Ztg.*, 1939, **63**, 754–755.)—It is usual to impregnate the sample of wood with calcium acetate solution before ashing prior to the determination of fluoride. It is now proposed to incorporate chromium acetate in the impregnating solution (a solution containing 6 per cent. of calcium acetate and 3 per cent. of chromium acetate is recommended.) More complete recovery of the fluorine and speedier ashing are claimed. The fluorine in the ash may be determined by distillation as silicon fluoride and subsequent titration as in Willard and Winter's method. S. G. C.

Microchemical

Spot Tests for Silver, Lead, Mercury, Uranium and Aluminium. E. A. Kocsis. (*Mikrochem.*, 1939, **27**, 180–184.)—The reagents used are benzopurpurin 4B, and bromophenol blue (Merck No. 8182) in 0·2 per cent. aqueous solution and morin (Merck No. 6098) in 0·2 per cent. alcoholic solution. *Silver* nitrate and benzopurpurin 4B give a brown ring with a red spot in the middle on filter-paper; *limit of identification*, 0·03 mg. of silver. The other ions do not give this reaction. The intensity of colour is lost on drying. *Lead* nitrate and bromophenol blue form on filter-paper a violet-red circle, surrounded by and encircling a number of colours; on drying, only the circle retains its brightness; *limit of identification*, 0·025 mg. lead; silver and copper ions interfere with this test. *Mercurous* nitrate gives red-brown colours with benzopurpurin 4B and bromophenol blue, which do not fade very much on drying and may be kept for several weeks; *limits of identification*, 0·04 mg. and 0·015 mg. *Mercuric* nitrate forms blue-green and yellow ochre colours with the two above-named reagents; the colours retain their intensity for several weeks; *limits of identification*, 0·025 mg. with benzopurpurin 4B and 0·02 mg. with bromophenol blue. *Uranium* nitrate gives a light brown colour with benzopurpurin 4B and a red-brown colour with bromophenol blue. Both colours lose their intensity on drying; *limits of identification*, 0·035 mg. with benzopurpurin 4B and 0·025 mg. with bromophenol blue. *Aluminium* sulphate forms a bright red-brown colour with benzopurpurin 4B, which is unchanged by drying; *limit of identification*, 0·005 mg. of aluminium. The morin test for aluminium may be made sensitive down to 0·001γ of aluminium by carrying out the test in non-fluorescent glass and observing the reaction in transmitted ultra-violet light. J. W. M.

Salts of Complex Cations applied to the Microscopic Detection of Anions. VIII. 1.2-Chloro-aquotetramminocobaltic Chloride. L. V. Yanowski and W. A. Hynes. (*Mikrochem.*, 1929, **27**, 161–164.)—The reagent, $[Co(NH_3)_4(H_2O)Cl]Cl_2$, was prepared by a modification of Werner's method (*Ber.*, 1907, **40**, 4817), and a saturated aqueous solution of the salt was employed. Characteristic crystals are formed only with pyro- and ortho-phosphate ions, from 1 per cent. solutions of the anions. With the former pyramidal masses form immediately (*limit of identification*, 67γ HPO_4^{--}); with the latter, spruce-like fronds develop in 5 to 7 minutes (*limit of identification*, 0·2 mg. $P_2O_7^{----}$). Non-characteristic crystalline precipitates are obtained with silicotungstic acid and alkali metal

salts of biniodate, dichromate and nitrite. Turbidities of varying densities are formed by phosphomolybdic and phosphotungstic acids and by dipicrylamine, as well as by the alkali metal salts of bisulphite, chromate, ferricyanide, ferrocyanide, iodate, metaphosphate, metavanadate, molybdate, orthovanadate, oxalate, paratungstate, phosphomolybdate, phosphotungstate, sulphite, tellurate, tellurite, tetraborate, tungstate, and xanthate ions. No reaction was obtained with 54 other anions that were tested. Five photomicrographs are given.

J. W. M.

Activation of Vanadium with Pyrocatechol. L. Szebelledy and M. Ajtai. (*Mikrochem.*, 1939, **26**, 72–74.)—Vanadium catalyses the reaction between *p*-phenetidine and potassium bromate, and the catalysis is activated by pyrocatechol. The sample is treated with 1 ml. of a 1 per cent. solution of pyrocatechol, 1 ml. of a 0·1 per cent. solution of *p*-phenetidine in hydrochloric acid and 1 ml. of saturated potassium bromate solution. The mixture is diluted to 5 ml. and compared, after a few minutes, with a blank. In presence of 0·001γ of vanadium the sample gives a violet colour after 5 minutes as compared with a slight pink in the blank. The limit of identification is 0·0005γ of vanadium. The interference of silver ions may be prevented by adding 10 cg. of sodium chloride, that of lead by adding 10 cg. of sodium sulphate, and that of iron by the addition of 5 cg. of sodium difluoride. J. W. M.

Physical Methods, Apparatus, etc.

Lead-sodium Alloy as a Drying Agent. H. Soroos. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 657–658.)—Lead-sodium alloy reacts only slowly with air or water, yet dries ether as completely as sodium wire and is less hazardous to handle in presence of inflammable liquids. The alloy is very brittle and can be prepared in any desired state of subdivision. A mixture of 90 parts of lead and 10·5 parts of sodium, corresponding with the ratio NaPb that yields the lowest and safest concentration of sodium providing an active and brittle product, is heated in an iron crucible fitted with a lid through which passes an iron stirrer. After the mass is liquid the crucible is allowed to cool at an angle of 45°, and the alloy is removed and stored in an air-tight container. When required for use it is coarsely ground in a mortar, but if rapid reaction is required it may be finely ground under a layer of the liquid to be dried. Unless this precaution is taken, absorption of water from an excessively moist atmosphere may cause the finely powdered alloy to ignite. Upon reaction with water the alloy disintegrates into a fine powder, and the sodium is effectively and quantitatively used. In addition to its convenience for handling and its efficacy, it has the advantage that residues are disposed of by the addition of water without violent reaction. It is made industrially as an intermediate in the manufacture of lead-tetraethyl. A. O. J.

Reviews

THE RAMAN EFFECT AND ITS CHEMICAL APPLICATIONS. By J. H. HIBBEN, with a Theoretical Discussion by J. H. HIBBEN and E. TELLER. Pp. 544. American Chemical Society Monograph; published by Reinhold Publishing Corporation. 1939. Price 66s. net.

Since the announcement by Sir C. V. Raman in 1928 of the peculiar scattering of light rays by molecules, nearly two thousand communications on the subject of Raman spectra have been published by chemists and physicists. The universal interest aroused springs from the fact that the theoretical discussions have led to far-reaching conclusions on the structure of molecules and on molecular symmetry. The chemical application of the study may be considered quite apart from the physical processes which give rise to Raman lines. It is one of the objects of this monograph to present the facts, and deductions from them, in so far as they interest chemists. It is beyond question that the Raman effect can be correlated with certain kinds of chemical binding between atoms. Two examples, taken at random, may be given. In ethylenic compounds the C = C link is associated with a frequency shift of 1600 to 1680 wave-numbers; the presence of a halogen derivative can be detected in a hydrocarbon mixture by means of the Raman shifts.

Chapters 3 to 6 deal with the theory of the Raman effect. While these are necessarily based on modern mathematical treatment, the method of presentation gives a clear picture of the processes involved, and with a little persistence it can be grasped readily. The rules which govern the appearance of Raman lines, their polarisation and the relation of these to the symmetry of the molecule are clearly set out.

For those who do not desire to study the theory but are interested in the application to inorganic and organic chemistry and to biochemistry, Parts II and III, forming the major portion of the volume, can be read independently of the theoretical aspects of Part I. For the busy chemist this is a fortunate circumstance, since he can use the book with advantage in attacking many chemical problems. For example, it is stated that the Raman spectrum shows citral to contain no α-form, whilst citronellal is a mixture of the α- and β-forms. Again, the Raman spectra of certain sugars, such as glucose, sorbose, xylose and others, do not show a Raman shift in the region 1600 to 1700 wave-numbers, and, as this is the region where the carbonyl frequency should appear, it is concluded that aldehydic or ketonic structures are absent from these substances. Hibben points out that the Raman effect offers great promise for investigating industrial problems and also in applied biochemistry. The reviewer agrees with this view, and would point out that the Raman effect and the complementary infra-red spectrum are now coming into the field of analytical chemistry. The volume is by no means difficult to read and is fully up to the high standard of this series of Chemical Monographs.

The bibliography is complete and is arranged alphabetically, but the index could be improved, in the reviewer's opinion, if a different system were adopted, namely, a general index giving page numbers. This is, however, a minor matter and in no way detracts from the excellence of the volume for study and reference.

J. J. Fox

THEORETICAL AND APPLIED ELECTROCHEMISTRY. By M. DE K. THOMPSON. Pp. xxi + 535. 3rd Edition. New York: The Macmillan Company. 1939. Price 22s.

The general plan of this book is similar to that of the second edition, published in 1925, but the subject-matter has been brought up to date without any expansion of the text. The first part is theoretical, and deals with electrolysis, dissociation and migration of ions, conductance, electrokinetic phenomena and polarisation. Part II includes sections on electro-analysis, plating, the extraction and refining of metals, electrolytic oxidation and reduction, the production of oxygen and hydrogen, primary and storage cells, applications of electrokinetic phenomena and corrosion. The final section is concerned with electric furnaces and their products, and includes electrothermic metallurgy. No single volume could be expected to deal extensively with each of the many applications discussed, but the author has succeeded in presenting a broad survey of electrochemical processes.

In the theoretical section facts and theories are given briefly and the reader must look up the references given in the copious footnotes in order to amplify the lecture-note type of information of the text. Indeed, these footnotes and the bibliography at the end of each chapter combine to enhance the value of this book for reference purposes.

By contrast, some sections in Part II contain a wealth of detail: dimensions of plant, operating conditions, diagrams, drawings, photographs and the like. The information was presumably made available to the author by the various companies to whom acknowledgment is made in the preface. The descriptions of some processes, for example, the manufacture of fused quartz, probably owe something to the patent literature—a source that is not always a true guide to current practice.

Descriptions of some new developments, for example the electric melting of glass, are so brief as hardly to warrant inclusion. There is a tendency to neglect sources other than American; among the tests for electroplating there is no mention of S. G. Clarke's B.N.F. Jet Test, and the information on the "salt spray" test is out of date. Much attention has been devoted to electrolytic oxidation and reduction processes in America of recent years, and a number of commercial processes are described in the book, among them the production of iodoform by oxidation and the reduction of glucose to give sorbitol and mannitol. Electrolytic analysis is allotted only six pages, and the analyst may not, therefore, expect to profit greatly from a perusal of this chapter, which deals only with general principles. The chapter on corrosion, new to this edition, begins with the statement that the American oil industry lost 175 million dollars in 1927 as a result of corrosion, but as only two pages are devoted to the subject, they might well have been omitted.

The book is well produced and misprints are few, but there is some careless usage of words. It must be one crystallite of graphite, not one molecule, that contains only 30 atoms (p. 421); electrolytic α brass has a micro-structure, not a crystal structure, different from cast brass of the same composition (p. 154).

The problems following each chapter, extended solutions to which are given at the end of the book, contribute towards an understanding of the subjects

discussed. Though primarily written for students, this book should be equally useful for reference purposes since a large part of it is devoted to practical industrial applications. R. C. CHIRNSIDE

FLUORESCENCE ANALYSIS IN ULTRA-VIOLET LIGHT. By J. A. RADLEY and JULIUS GRANT. 3rd Edition. Pp. 424 + 28 photographs. London: Chapman & Hall. 1939. Price 22s. 6d.

Judging by the number and range of papers regularly published on fluorescence analysis there is no lack of interest in this subject. In recent years there has been no outstanding advance; but extension of application is evident in almost every branch of applied chemistry. There is thus ample justification for the appearance of this new edition which brings the subject-matter right up to date.

The general arrangement follows that of the two previous editions, accounts of which have already been recorded (ANALYST, 1934, **59**, 209; 1936, **61**, 215). Each of the first 19 chapters contains the material of the last edition (slightly revised and edited), together with additional matter published within the last few years. The final chapter is almost wholly new and comprises 17 pages dealing with recent work in the dyestuffs industries in connection with the laws of fluorescence, classification or identification of dyes, accelerated fading and the detection of faults. Nine more photographs are included.

The additions result in an increase of about one-third in the size of the book and quantitatively it may be said that 30 per cent. more pages have been provided for a 7 per cent. increase in price. Yet qualitatively the new material is more valuable than the old, for exaggerated claims, referred to in the review of the last edition as occurring in much early work, have been succeeded by more cautious estimates.

The authors have now on three occasions provided an admirable, up-to-date collection of the published work on fluorescence analysis. The latest volume approaches the limiting size for convenience, and for a subsequent edition it may be necessary to delete some of the information and references now included to make room for newer work. The task of separating the chaff from the grain will be difficult; but it is hoped that the authors will not shirk this winnowing, as it would improve the harvest for the increasing number of people who utilise the seed that has been garnered for them. J. R. NICHOLLS

TECHNICAL METHODS OF ORE ANALYSIS FOR CHEMISTS AND COLLEGES. By A. J. WEINIG and W. P. SCHODER. Based upon the text by A. H. Low. Eleventh Edition. Pp. x + 325. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1939. Price 22s. 6d.

All analysts engaged in metallurgical practice will welcome the new edition of the late Dr. Low's well-known manual, revised by A. J. Weinig, Director, and W. P. Schoder, Chemist, of the Experimental Ore Dressing and Metallurgical Plant of the Colorado School of Mines.

The greater part of the text is a revised and up-to-date reproduction of Dr. Low's excellent work, and since this is (or should be) on the bookshelf of every metallurgical laboratory, further commendation appears superfluous. The reviewer's remarks are therefore confined to the new features of the present edition.

The introductory chapters of the former editions on apparatus, electrolysis, and logarithms have been omitted and replaced by a 24-page chapter entitled "Semi-micro Methods." This consists of a collection of 42 qualitative spot tests for the most important elements, preceded by an illustrated description of the apparatus required, and supplemented by two handsome coloured plates showing the result of the colour test in each case. These tests are intended to be carried out on a drop withdrawn from the assay solution.

One new chapter—on beryllium—has been added to those devoted to the quantitative determination of the various elements. The reviewer is gratified to find that the method described by the authors for the determination of beryllium is based on the process he advocated as the simplest for the separation of beryllium from aluminium, namely, fusion of the ammonia precipitate with sodium carbonate (ANALYST, 1936, **61**, 235).

Each of the chapters on individual elements now comprises a table giving the most important minerals of the element under discussion, with useful data on properties and associated elements and reagents available for their decomposition. The table on cadmium minerals cites only the rare mineral greenockite; in the reviewer's opinion, it would be preferable to include zinc blende which, though not a cadmium mineral, is the only cadmium ore of commercial importance. Again, the table on silicate minerals does not mention quartz, by far the most abundant source of silica. Zinc blende might have been added to the sulphur minerals, since it is extensively used for the manufacture of sulphuric acid.

It may be suggested that an account of the colorimetric determination of small amounts of bismuth would form a most useful addition to the bismuth chapter.

Among the few misprints that have escaped proof-reading may be noted the atomic weight of hydrogen, in the table inside the back-cover (1·081 for 1·0081); and the gravimetric factors for zirconium pyrophosphate (p. 308). The formula of this compound should read ZrP_2O_7 (not $Zr_2P_2O_7$), and the factors for Zr and ZrO_2 be corrected accordingly. W. R. SCHOELLER

A TEXT-BOOK OF QUANTITATIVE INORGANIC ANALYSIS. Theory and Practice. By ARTHUR I. VOGEL, D.Sc., D.I.C., F.I.C. Pp. xix + 856. With 4 plates and 130 diagrams. London: Longmans, Green & Co. 1939. Price 18s.

In this book the balance between classical methods, of importance for their instructional value, and those required in commercial work, is struck and maintained in a way that should appeal both to teachers and to those engaged in the practice of analytical chemistry.

In the theoretical section (193 pp.) general theory receives full mathematical treatment and is illustrated by fully-worked examples of the several laws. This is followed by the theory of volumetric and gravimetric analysis, the subject being taken from first principles to its most recent stage of development. Technique (84 pp.) is treated first in general, and then with detailed description of the apparatus, calibrations and manipulation required for volumetric and gravimetric analysis. The chapter on volumetric analysis (195 pp.) contains, in addition to the usual elementary matter, descriptions and exercises on adsorption indicators and methods utilising mercurous perchlorate, ceric sulphate, manganic sulphate, titanous sulphate, liquid amalgams and chloramine-T.

The section on gravimetric analysis (197 pp.) covers simple determinations, systematic analysis (in which 13 of the commoner "rare" elements have not been overlooked), electrolytic determinations, simple separations and analysis of complex materials such as alloys and minerals. The critical discrimination and modern outlook of much of this and the preceding section bear more resemblance in style to that of a work of reference than a text-book; this adds interest for the chemist engaged in general analysis. In selecting methods of determination full use has been made of recently published original papers, including some from the pages of THE ANALYST. For all elements a wide choice of procedure is offered.

Colorimetric Analysis receives 62 pages, of which 29 are devoted to theory and instruments; procedures are described for 19 characteristic ions, and a table of reference is provided for 26 other elements and radicals. Gas Analysis (46 pp.) describes and illustrates the use of the Hempel, Bunte, Orsat, Ambler, and Bone-Wheeler apparatus and the Lunge nitrometer. An appendix (65 pp.) contains, in addition to all the usual matter, a table of buffer solutions for standardisation of *p*H measurements, a comprehensive bibliography of analytical chemistry and a table of *five*-figure logarithms. The index (14 pp.) is rendered easy of reference by heavy type for main headings and a system of abbreviations to indicate the class to which a determination belongs.

This work, which is remarkably free from errors, is likely to set a new standard for text-books of quantitative inorganic analysis. F. L. OKELL

Publications Received

PHYSICO-CHEMICAL METHODS. Vol. I. MEASUREMENTS AND MANIPULATIONS. Vol. II. PHYSICAL PROPERTIES. 3rd Ed. By J. REILLY and W. NORMAN. London: Methuen & Co. 1940. Price £4 4s. net.

AN INTRODUCTION TO BIOCHEMISTRY. 2nd Ed. By W. R. FEARON. Pp. xii+ 475. London: William Heinemann (Medical Books), Ltd. 1940. Price 17s. 6d. net.

PRACTICAL PHARMACEUTICAL CHEMISTRY. 4th Ed. By F. N. APPLEYARD and C. G. LYONS. Pp. viii + 174. London: Sir Isaac Pitman & Sons, Ltd. 1939. Price 6s. 6d. net.

METALLURGICAL ANALYSIS AND ASSAYING. By J. S. REMINGTON and F. L. JAMESON. Pp. vii + 101. London: The Technical Press, Ltd. 1939. Price 5s. net.

SULPHATED OILS AND ALLIED PRODUCTS. Pp. 167. London: A. Harvey. 1939. Price 12s. 6d. net.

LES PARFUMS NATURELS. By Y. R. NAVES and G. M. MAZUYER. Pp. xvi + 398. Paris: Gautiers Villars. 1939. Price 120 fr.