THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society with the Food Group of the Society of Chemical Industry was held on Wednesday, February 3rd, 1937, at the Chemical Society's Rooms, Burlington House. It was held in two sessions, at the first of which the chair was taken by Dr. G. Roche Lynch, President of the Society, and at the second by Dr. L. H. Lampitt, in the absence of the Chairman of the Food Group.

Certificates were read in favour of:—William Mitchell Cameron, James Laurence Campbell, B.Sc., Frank James Griffin, B.Sc., Herbert Clewin Griffith, Robert Edmund Richard Grimmett, M.Sc., F.N.Z.I.C., Eric Kennedy, B.Sc., A.I.C., Robert Hay McKinlay, F.I.C., John Aitken Macnair, F.I.C., Geoffrey William Martin, Enid Marian Pope, B.A., B.Sc., Archibald Rayner, B.Sc., F.I.C., William James South, Edward Taylor-Austin, A.I.C., John Ezra Woodhead, B.Sc., F.I.C., Ph.C., James Hunter Young, B.Sc., A.I.C.

The following were elected members of the Society:—Granville Hubert Clarke, Leonard Cartlidge Dutton, A.I.C., John Charles Giblin, B.Sc., A.I.C., Ronald William Gillham, Ph.C., Ronald Murray Hamilton, Walter Thomas Lunt, B.Sc., A.I.C., William Douglas McFarlane, M.A., Ph.D., William Stewart Patterson, Ph.D., M.Sc., F.I.C., Thomas Charles Williams, B.Sc., A.I.C., George Henry Wray.

The Meeting was devoted to a discussion on

THE LESS-KNOWN CONSTITUENTS OF MILK AND THEIR EXAMINATION.

The following papers were read and discussed:—"Some Minor Component Acids in Milk-fat and their Possible Significance," by Professor T. P. Hilditch, D.Sc., F.I.C.; "The Oxidation-Reduction Systems in Milk," by R. T. S. Twigg, B.Sc.; "Some Recent Work on the Lipase and Phosphatase of Cow's Milk," by Professor H. D. Kay, O.B.E., Ph.D., D.Sc., E. C. V. Mattick, M.Sc., Ph.D., and S. J. Folley, M.Sc., Ph.D.; "Present Knowledge of the Minor Nitrogenous Constituents of Milk," by J. H. Bushill, D.Sc., A.I.C., L. H. Lampitt, D.Sc., F.I.C., and D. F. Filmer, B.Sc.; and "The Estimation of Catalase in Milk," by E. B. Anderson, M.Sc., F.I.C., and R. MacWalter, Ph.D.

NORTH OF ENGLAND SECTION

THE Twelfth General Annual Meeting of the Section was held in Manchester on February 6th, 1937. The Chairman (A. R. Tankard) presided over an attendance of twenty-eight.

The Secretary presented the report and financial statement, which were adopted.

The following appointments for the coming year were made:—*Chairman*, A. R. Tankard; *Vice-Chairman*, Prof. T. P. Hilditch; *Committee*, W. F. Elvidge, J. Evans, S. E. Melling, Miss M. Roberts, C. A. Scarlett, J. R. Walmsley; *Honorary Auditors*, U. A. Coates, J. W. H. Johnson; *Honorary Secretary and Treasurer*, J. R. Stubbs.

The Chairman delivered the Annual Address, entitled "Chemical and General Scientific Control for Local Authorities."

The following paper was read and discussed:—"Notes on the Addendum, 1936, to the British Pharmacopoeia, 1932," by J. R. Walmsley, F.I.C.

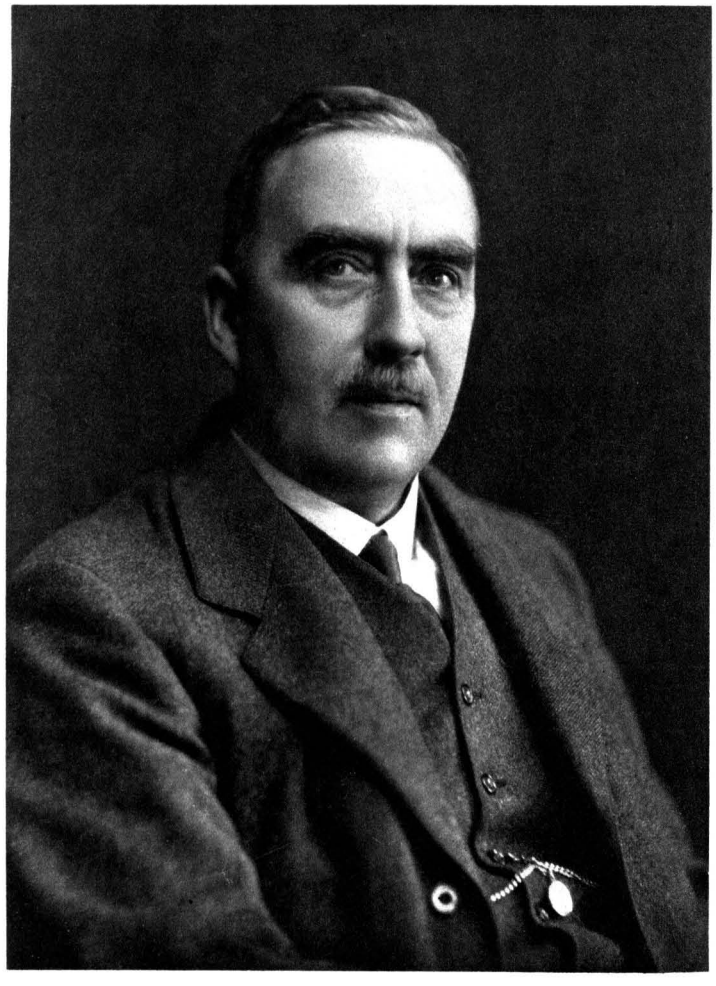
Obituary

PERCY ANDREW ELLIS RICHARDS, F.I.C.

ON the 22nd of December, 1936, there passed from our midst one who gave of his best to our Society and who in his time bore its highest honour, one who came only just a little too late to be considered among its actual founders, but whose work on its behalf is unsurpassed for enduring and consistent loyalty. For seventeen years he was one of our Honorary Secretaries, having as partners in this post the late A. Chaston Chapman and then E. Richards Bolton. At the end of this period his services were recognised by promotion to the Presidential chair. Afterwards, as Past President, he still held dear the interests of the Society and worked for it as long as strength was given him.

Born in 1868, he was educated at St. Paul's School and King's College, London, and studied analytical chemistry under the late Professor C. W. Heaton, having as fellow students Edward Russell and the late S. A. Vasey. With Vasey he was afterwards associated in joint work for *The Lancet* Laboratory. Heaton held the appointment of Lecturer in Chemistry and Physics at Charing Cross Hospital, and was succeeded in it by Richards. On the passing of his chief Richards set up in practice as consulting and analytical chemist, and was soon appointed Public Analyst for the parish of St. Martin-in-the-Fields. When various parishes were united to form the City of Westminster he remained as one of the three Public Analysts for the City, jointly with Col. C. E. Cassal and Mr. C. H. Cribb. A few years later he was appointed Public Analyst for the borough of Hammersmith. For many years he acted as Honorary Analyst to Charing Cross Hospital, and his interest in medical chemistry and toxicology led to his being consulted in some famous cases.

During his many years in practice he was responsible for work upon preservatives in imported meat, on the "facing" of rice, and on vinegar, for the Local



P. A. Ellis Richards

Government Board—now the Ministry of Health—the results of which are embodied in official communications. He also served as the Society's representative on the Departmental Committee on Preservatives and Colouring Matters in Food, appointed by the Minister of Health in 1923, and in 1925 as a member of the Departmental Committee on Improvers in Flour. In 1906 he served on the Advisory Committee on Drugs and acted as Honorary Secretary to this Committee.

Richards was a Fellow of the Chemical Society, and was also a loyal and active Fellow of the Institute of Chemistry, on the Council of which he served for two periods—1901 to 1904, and 1914 to 1917; from 1906 to 1909 he acted as Honorary Auditor to the Institute, and in 1910 was appointed Examiner in Branch E, which post he held for the usual four years.

To dwell upon his services to our Society, or to recount the many papers that he contributed to THE ANALYST, is not necessary here, for they are well known to us. His communications to *The Lancet* and other journals are, perhaps, less familiar because they deal with subjects somewhat removed from the usual work of Public Analysts. He wrote upon the saline waters of Boston Spa and of Salsomaggiore, as well as upon the determination of platinum in alloys and on the determination of iron in animal organs. It is interesting to recall that he was associated with Dr. William Hunter in researches on pernicious anaemia, especially with regard to the accumulation of iron in the liver, kidneys and spleen in this disease; he carried out large numbers of determinations of iron in these organs.

Analytical chemistry, though the chief part of his work, was yet only a part. As a teacher he held the post at Charing Cross Hospital already mentioned, and subsequently that of Lecturer in Chemistry and Metallurgy at the Royal Dental Hospital, combining these with his appointment as Professor of Chemistry at Queen's College, London. His merits as a teacher are recalled with gratitude by the writer and all the old students of Charing Cross and the Royal Dental Hospitals and of Queen's College; his kindly and painstaking manner endeared him to us all, no less than his powers of lucid exposition of the more difficult subjects evoked our admiration. In his early days he wrote a small textbook on practical chemistry for medical students, which, when subsequently enlarged to cover a wider syllabus, became probably the best-known work on the subject in medical schools.

It might be thought that these two spheres of activity were enough to fill one life, but in addition to serving on various councils and committees at the institutions wherein he taught, he found time to apply, very successfully, his financial ability to the service of Queen's College as Bursar and the Royal Dental Hospital as Honorary Treasurer. These duties, so many and so varied, he performed very conscientiously and with distinction; if only he had spared himself a little, he might, perhaps, never have suffered that breakdown in health which robbed us of his presence.

His last years were full of a wistful longing to get back to the things of the practical scientific world. Those of us who could sense this tried to make him feel that, although he was no longer active within our circle, he was still a valued member of it and very much in our thoughts. But the busy world left us little time to do more than outline to him the ever new happenings within it, though the

eagerness with which he followed the tale and enquired about his friends showed all too plainly that he still had their welfare and that of our profession very much at heart. During these years what weighed most heavily upon him was his enforced idleness at a period when many notable advances were being made in the branch of knowledge which he had made his own. In these advances he was well equipped to take a leading part, and it is sad to ponder upon the loss of all that his co-operation might have brought us.

The unstinted and self-denying service which he rendered to chemistry has earned the lasting gratitude of chemists. F. W. EDWARDS

The Determination of Lead in Water

BY J. W. HAWLEY, B.Sc., F.I.C., A.M.I.CHEM.E., AND W. WILSON, F.I.C.

(*Read at the Meeting of the Scottish Section, November* 19, 1936)

VARIOUS methods have been proposed from time to time for the analytical determination of lead in drinking water, the majority based on its colorimetric estimation as sulphide. Others include its precipitation as chromate,[1] followed by the determination of the latter by means of potassium iodide and thiosulphate, and the use of its peroxide,[2,3] formed chemically or by electrolysis, to produce the coloured hydroxy-tetramethyldiaminodiphenylmethane compound. The most recently introduced methods[4] employ organic reagents, notably dithizone—diphenylthiocarbazone.

[Technical Paper No. 4 of the Water Pollution Research Board (a publication of the greatest value to anyone interested in the problem) gives a summary of existing knowledge up to 1934. It would appear that in many cases the methods of analysis might give rise to serious error from the presence in the waters examined of other metals and substances.]

It is with amounts of lead of the order of 0·01 to 0·05 part per 100,000, generally in peaty water, that we have been mainly concerned, and the following note is a description of methods we have found satisfactory. These methods have now been in use for nearly two years.

For the detection of lead in water, the customary acetic acid and hydrogen sulphide test serves, provided that not less than 0·02 part of lead per 100,000 is present, that the sample is colourless or nearly so, and that it is compared with a control using a column of depth not less than 12 in. When the water is discoloured by vegetable matter, amounts of the order of 0·05 part of lead per 100,000 cannot always be detected with certainty. Such waters, particularly when the *p*H is below 7, may contain iron in amount sufficient to make the result uncertain, while the hydrogen sulphide exerts a bleaching action on the organic matter, so that the solution under test may actually appear lighter than the untreated control. In such cases, however, the dichromate test will generally demonstrate the presence of lead, although the opalescence may take some time to develop.

FIRST METHOD.—This consists simply of the relevant portions of the method devised by Francis, Harvey, and Buchan[5] for the determination of lead in urine.

The following solutions are required:—(1) Citric acid solution, 10 per cent.; (2) copper sulphate solution, 0·8 per cent.; (3) conc. sulphuric acid; (4) masked methyl orange indicator; 1 g. of methyl orange and 1·4 g. of xylene cyanol F.F. dissolved in 500 ml. of 50 per cent. alcohol; (5) ammonia, sp.gr. 0·880; (6) conc. nitric acid; (7) ammonium acetate solution, 10 per cent.; (8) potassium cyanide solution, 10 per cent.; (9) ammonia, 6 *N* (approx.); (10) sodium sulphide solution: sodium sulphide pure crystals 50 g., glycerin 50 g., water to 250 ml.; this solution is diluted with an equal bulk of water just before use. The reagents should all be of analytical reagent quality.

To 250 ml. of the sample contained in a conical flask are added 3 ml. of citric acid solution, 3 ml. of copper sulphate solution, 2 ml. of concentrated sulphuric acid and 2 to 3 drops of indicator. Concentrated ammonium hydroxide (sp.gr. 0·880) is now run in until the red colour gives place to purple and finally to a neutral grey. The addition of one or more drops produces a green tint, and the *p*H of the solution is then between 4 and 5. Hydrogen sulphide is now passed through the solution for an hour.

After standing for 15 to 30 minutes the liquid is filtered through an 11-cm. Swedish paper (No. 1. F), and the precipitate is washed twice with a saturated solution of hydrogen sulphide. The precipitate and paper are then transferred to a tall 250-ml. beaker. Nitric acid (1 to 2 ml.) is added to the original flask, which is then heated over a rose burner, and the acid with subsequent washings are added to the paper in the beaker. This recovers any precipitate still adhering to the walls of the flask. The paper containing the mixed sulphides is now destroyed by a wet combustion. Four or five ml. of nitric acid and 3 ml. of sulphuric acid are added to the contents of the beaker, which is then covered with a watch-glass and heated on the hot plate until a clear solution is obtained, further additions of nitric acid being made if necessary. When the oxidation is complete, the watch-glass is removed and the heating is continued until the excess of sulphuric acid has been expelled, the last traces being driven off by gentle blowing while the beaker is still hot.

The residue of mixed sulphates is treated with 10 ml. of water and conc. ammonia (sp.gr. 0·880) added dropwise until the colour of the solution is a deep blue; 25 ml. of water containing 1·5 ml. of nitric acid are then added, and the solution is ready for electrolysis.

The electrolysis is conducted with the electrodes and under the conditions prescribed by Francis, Harvey and Buchan, *i.e.* the electrodes are of platinum-iridium (25 per cent. of iridium). The anode is a cylinder 1 cm. deep and of 1 cm. diameter, and the cathode is $1\frac{1}{2}$ cm. square; wires 12 cm. long are attached to both. The conditions are: temperature, 70 to 80° C.; voltage, 1·5 to 2; current density, 0·3–0·4 amp. per 100 sq.cm.; speed of rotation of anode 1500–2000 r.p.m.; period of electrolysis 1 hour.

We have found the following mechanical arrangement satisfactory:—The electrode wires pass through 2 small holes, 4 cm. apart, drilled in the watch glass which covers the tall 250-ml. beaker, that of the anode to the customary rotating holder, that of the cathode to a fixed holder.

Each rotating anode is driven directly from its own pulley fixed on a horizontal

countershaft, which in turn is driven by a small series-wound motor. The speed of the motor is controlled by a variable resistance composed of a bank of lamps, and is measured by means of a revolution counter connected with the spindle of the motor by wheel and worm gearing.

A 4-volt accumulator connected with a distributing board supplies the current for electrolysis. On the board are mounted variable resistances and switches for controlling the currents passing to the electrodes, each pair of which has its own resistance and multiple switch. The last-named serves as an on/off switch and also permits of the insertion of a voltmeter and an ammeter in the circuit of any cell for test purposes without interrupting the electrolysis.

When the electrolysis is completed, the deposit of lead peroxide is dissolved by transferring the anode, after washing, to a Nessler glass containing about 10 ml. of water to which 2 to 3 drops of nitric acid and a crystal of potassium oxalate have been added.

From the appearance of the deposit an opinion can be formed of the approximate amount of lead present, and the entire solution or an aliquot portion can be used for the determination. The volume of the solution taken should be such that the amount of lead present is between 0·035 and 0·065 mg.

To the liquid under test are added 10 ml. of ammonium acetate solution, 2 ml. of potassium cyanide solution, 5 ml. of 6 *N* ammonia, and then water to 50 ml. The whole is mixed and allowed to stand for 2 to 3 minutes, after which 2 drops of sodium sulphide solution are added, the solution is again mixed, and the tint is compared immediately with standards.

The range of standards is prepared in a similar manner, varying volumes—0·5 to 1·5 ml. by increments of 0·2 ml.—of standard lead solution (1 ml. = 0·05 mg. of lead), with the appropriate addition of nitric acid and potassium oxalate, taking the place of the liquid under test.

It is essential that the sample and standards be prepared under as nearly identical conditions as possible, both as regards the order of addition of reagents and the nature and quantity of electrolyte present.

A control is carried out in exactly the same manner, but using distilled water instead of the sample, so that the necessary correction for lead present in the reagents, etc., can be made. This correction is small and should not exceed 0·2 ml. of standard lead solution.

Having regard to the exhaustive investigations made by the original authors numerous check experiments were considered superfluous. A few results are given below.

Water	Lead Parts per 100,000		Remarks
	Added	Found	
Distilled	Nil	Nil	"blank," 0·0012, 400 ml. used
Distilled	0·011	0·009	400 ml. used
Reservoir A	Nil	Nil	"blank," 0·0012, 400 ml. used
(Oxygen absorbed in	Nil	Nil	"blank," 0·0018, 400 ml. used
4 hours, 0·39 part)	0·014	0·014	
	0·014	0·014	
	0·030	0·026	
	0·030	0·032	

This method has various advantages—gain of lead is unlikely, and there is little risk of loss, as the sulphide is precipitated directly with a large excess of copper. The wet combustion, though time-consuming, needs little or no attention. Electrolysis gives the lead free from interfering elements likely to be present, and in a form suitable for easy estimation. The separation of sulphate with alcohol is unnecessary, and the "blank" is low.

On the other hand, there are the troubles attendant on the filtration of relatively large volumes of a saturated solution of hydrogen sulphide—particularly noticeable in any building not used exclusively as a laboratory. The apparatus is expensive, especially the platinum portion, and although costly electrical instruments are not required, a low resistance ammeter is desirable. In addition, the operator must give considerable attention to the electrolysis.

SECOND METHOD.—This is the method we generally employ, as it is more suitable for batch working.

The solutions required are those previously described with the exception of No. 2 (copper sulphate). Potassium chlorate is also needed.

Two hundred and fifty ml. of the sample, acidified with 2 ml. of hydrochloric acid, are evaporated to about 5 ml. in a silica basin (or beaker) and allowed to cool. A few crystals of potassium chlorate and 1 ml. of conc. hydrochloric acid are then added, the basin is covered, and the contents are allowed to simmer for a short time over a rose burner. The cover is removed, and the sides of the basin are rinsed with the acid liquor and washed down with boiling water. A further 1 ml. of conc. hydrochloric acid is added, and the solution is boiled until free from chlorine. The hot solution is then filtered through a 5·5-cm. No. 41 Whatman paper into a 50-ml. conical flask, and the basin and paper are washed with boiling water. The total volume of the filtrate should not exceed 25 ml.

One ml. of citric acid solution and one drop of masked methyl orange are added to the cold filtrate, and ammonia (0·880) is next run in until the red colour of the indicator changes to purple, when the neutralisation is continued with 2 *N* ammonia until the purple colour changes to a grey tint and finally to green. Care must be taken that the final change to green is effected with a single drop of ammonia. If the end-point is overstepped, hydrochloric acid must be added to restore the purple colour, and then 2 *N* ammonia until the proper end-point is reached. Hydrogen sulphide is next passed through the solution for 45 minutes.

The precipitate is allowed to settle, the solution is filtered through a 5·5-cm. Swedish paper (No. 1. F), and the flask and precipitate are washed twice with a saturated solution of hydrogen sulphide. The lead sulphide on the paper is dissolved in 1 ml. of conc. nitric acid, the filtrate being received in a 100-ml. beaker. To ensure the complete removal of the precipitate from the flask, a few drops of nitric acid are added, and the contents are heated gently over a rose burner, the acid and subsequent washings being passed through the filter. When washing is completed 10 drops of conc. sulphuric acid are added to the contents of the beaker, which are then evaporated to dryness on the hot plate, and allowed to cool. Five ml. of ammonium acetate solution are added, the beaker is covered, and the contents, after boiling for a few minutes, are filtered through a 5·5-cm. No. 41 Whatman paper into a 50-ml. Nessler glass. A further 5 ml. of ammonium acetate solution

are added to the beaker, and the liquid is boiled and filtered through the same paper, which is then washed with boiling water containing a little ammonium acetate until the volume of the filtrate is about 30 ml.

Whether the entire volume of the filtrate or only an aliquot part should be used for estimation can generally be decided from the appearance of the sulphide precipitate. As stated earlier, the volume of solution taken should be such that the amount of lead present lies within the limits 0·035 and 0·065 mg. When an aliquot portion is taken, sufficient ammonium acetate solution should be added to bring the total amount in the Nessler cylinder up to 10 ml. To the liquid under test are added 2 ml. of potassium cyanide solution, 5 ml. of 6 *N* ammonia, and water to 50 ml. The whole is mixed and allowed to stand for 2 to 3 minutes. Two drops of sodium sulphide solution are next added, the solution is again mixed, and the tint is compared immediately with standards.

To prepare the range of standards, varying volumes of 0·5 to 1·5 ml. by increments of 0·2 ml. of standard lead solution (1 ml. = 0·05 mg. of lead) are added to Nessler cylinders, each containing 10 ml. of ammonium acetate solution. Additions of potassium cyanide and ammonia, etc., are made in the manner just described, the sample and standards being prepared under as nearly identical conditions as possible.

A control, using distilled water to replace the sample, enables the necessary correction to be made for lead present in the reagents and gained from the apparatus, etc.

The correction (blank) in this method is greater than in the first method, but should not exceed 0·4 ml. of standard lead solution.

In a series of tests the following results were obtained:

Water	Lead Parts per 100,000		Remarks
	Added	Found	
Distilled	0·008	0·010	"blank," 0·008
	0·011	0·009	"blank," 0·007
	0·020	0·021	
	0·028	0·026	
	0·038	0·038	
Reservoir A (oxygen absorbed in 4 hours 0·39 part)	0·014	0·017	"blank," 0·008
	0·014	0·016	"blank," 0·007
	0·030	0·031	
	0·030	0·025	
Composite (oxygen absorbed in 4 hours 1·0 part)	0·010	0·009	"blank," 0·005
	0·014	0·019	
	0·020	0·023	
	0·039	0·035	
	0·048	0·051	
Water containing lead (oxygen absorbed in 4 hours 0·44 part)	Nil	0·012	"blank," 0·008
	0·006 (0·018)	0·016	500 ml. used
	0·012 (0·024)	0·024	
	0·018 (0·030)	0·030	
	0·024 (0·036)	0·040	

In this method it is only necessary to filter small volumes of hydrogen sulphide water, and, as the precipitated lead sulphide is dissolved from the paper, the wet combustion is merely that of the small amounts of paper fibre which have become detached by the acid and wash liquors. In the presence of much zinc or iron the electrolytic method is necessary.

THIRD METHOD.—This consists of a combination of the two preceding methods and is useful when lead and copper are present together. The procedure adopted follows that of the second method as far as the precipitation and filtration of the sulphides. The paper and precipitate are then transferred to a 250-ml. tall beaker, and a wet oxidation is carried out as in the first method. The resulting solution is electrolysed without previously coating the cathode with copper. So far we have not examined the influence (if any) of the absence of a preliminary copper deposit on the cathode, but the separation appears to be satisfactory. When electrolysis is completed the anode is removed and any solution adhering to it is washed back into the beaker. The deposit of lead peroxide is then dissolved, and the lead is determined in the usual way.

The copper which has separated on the cathode during electrolysis dissolves in the electrolyte on breaking the circuit. The electrode is removed and washed. Two ml. of hydrochloric acid are added to the beaker, and the contents are evaporated to dryness on the hot plate. The residue is taken up with dilute hydrochloric acid and the copper is estimated colorimetrically as ferrocyanide.

As described, these methods give satisfactory results when the amount of lead present is 0·01 part (or more) per 100,000. With smaller amounts not less than 500 ml. of the sample should be taken.

SUMMARY.—Two methods are described for the separation and determination of lead in drinking water.

(1) *Electrolytic Method.*—(*a*) The lead is precipitated directly as the sulphide in the presence of a large excess of copper, the solution being previously buffered to a *p*H value between 4 and 5.

(*b*) The mixed sulphides are filtered off and washed with saturated hydrogen sulphide water.

(*c*) The paper containing the sulphides is destroyed by a wet combustion.

(*d*) *The lead is separated from this solution as peroxide by electrolysis.*

(*e*) The deposited lead peroxide is dissolved from the electrode and the lead estimated colorimetrically as the sulphide.

This method is recommended when the highest degree of precision is desired and when the water is further contaminated by other metals.

(2) *Concentration Method.*—(*a*) The water is acidified and concentrated to a small volume.

(*b*) The organic matter in the concentrated water is oxidised by potassium chlorate in the presence of hydrochloric acid.

(*c*) The solution is buffered to a *p*H value 4 to 5, and the lead is precipitated as sulphide.

(*d*) The sulphide is collected on a filter-paper, washed, and dissolved in conc. nitric acid.

(*e*) The solution is evaporated to dryness with sulphuric acid to destroy any filter-paper fibres present.

(*f*) The lead sulphate is dissolved by boiling with a solution of ammonium acetate, and, after filtration, the lead is estimated colorimetrically as sulphide.

This method is recommended where a large number of samples have to be examined, since determinations can be made conveniently in batches of from six to eight. By connecting the flasks in series, one Kipp apparatus suffices for "gassing."

This method should not be used in the presence of zinc or of much copper or iron.

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2. A. Trillat, *Compt. rend.*, 1903, **136**, 1205.
3. A. Seiser, A. Necke and H. Müller, *Z. angew. Chem.*, 1929, **42**, 96.
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COUNTY LABORATORY
DUMFRIES

The Determination of Benzoic Acid

BY F. W. EDWARDS, F.I.C., H. R. NANJI, PH.D., D.I.C., F.I.C., AND M. K. HASSAN, M.SC.

(*Read at the Meeting, November* 4, 1936)

PART I. MODIFICATION OF NICHOLLS'S METHOD

THE partial conversion of benzoic acid into salicylic acid by hydrogen peroxide was first noticed by Hanriot,[1] but no attempt was made to apply the test—which is often described as Jonescu's test—to the determination of this acid until Nicholls[2] studied exhaustively the optimum conditions, particularly those under which the proportion of salicylic acid produced was constant. Nicholls found that:—(1) Small quantities of benzoic acid were readily oxidised to salicylic acid by hydrogen peroxide in slightly acid solution in the presence of iron salts, and that rise of temperature enhanced the rate of oxidation. (2) Under standardised conditions of concentration of mineral acid, hydrogen peroxide and ferric chloride, the proportion of benzoic acid converted was about 12 per cent., and this proportion was fairly constant up to a maximum concentration of benzoic acid (5 mg. in 15 ml.).

The amount of salicylic acid formed was determined either by the ferric salicylate test or by Jorissen's test. In applying the ferric salicylate test after oxidation it is essential to regulate the acidity within a narrow limit—about 0·002 *N*—since the depth of colour and the tint vary appreciably with the acidity of the solution. Nicholls added a fixed amount of alkali after oxidation and filtered the solution, this procedure being adopted to remove the bulk of the iron

salt, which would otherwise interfere in the colorimetric stage, as well as to regulate the acidity of the filtrate. Whilst we obtained fairly satisfactory results when working on pure benzoic acid, we were not always successful in getting the proper violet tint in dealing with extracts of the acid from food products, probably because of the difficulty of adjusting the acidity of the final solution.

We therefore attempted to modify the method so as to avoid the necessity of regulating the acidity. The procedure which we found very successful was to extract the salicylic acid from the cooled oxidation mixture by means of ether and, after removal of the solvent, to dissolve the residue in 10 per cent. alcohol and determine the salicylic acid colorimetrically as ferric salicylate. The *p*-hydroxy-benzoic acid and possibly dihydroxy-benzoic acids, which are simultaneously formed, do not interfere if the iron solution used in the colorimetric stage of the process is distinctly acid (see p. 179). The procedure also eliminates the necessity for a blank test, the colour match obtained by using a salicylic acid standard in 10 per cent. alcohol being quite satisfactory.

We have also made a few other comparatively minor modifications in order further to standardise the method, and these may be noted here:—(i) The oxidation is carried out in a distinctly acid solution by the addition of 5 ml. of 0·1 *N* sulphuric acid prior to oxidation; this prevents the possibility of precipitation of the iron salt before the oxidation is complete. (ii) The solution is heated by immersion in a boiling water-bath for 15 minutes, this being found the optimum time (see Table I). (iii) The strength of hydrogen peroxide is doubled, as this gives a definite increase in the yield of salicylic acid under our conditions.

In Table I are recorded the results of experiments wherein 5 mg. of benzoic acid were oxidised after addition of 5 ml. of 0·1 *N* sulphuric acid, time of heating and concentration of hydrogen peroxide being varied. The optimum concentration of hydrogen peroxide is therein shown to be 1 ml. of 0·2 per cent. in the 15 ml. of reaction mixture, and 15 minutes' heating is shown to be the period for the maximum yield of salicylic acid.

TABLE I

Benzoic acid taken mg.	Time of heating Minutes	Salicylic acid found: 1 ml. 0·1 per cent. hydrogen peroxide mg.	1 ml. 0·2 per cent. hydrogen peroxide mg.	1 ml. 0·4 per cent. hydrogen peroxide mg.
5	3	—	0·39	—
5	5	0·29	0·41	0·41
5	9	0·32	0·44	0·44
5	12	0·33	0·45	—
5	15	0·35	0·46	0·41
5	18	—	0·46	—

The modified method found satisfactory for foods and drugs is as follows:

REAGENTS REQUIRED.—(i) *Iron reagent A for oxidation*: a solution of 2·7 g. of anhydrous ferric chloride in 13 ml. of *N* sulphuric acid made up to 100 ml. with water; (ii) 0·2 *per cent. hydrogen peroxide solution* prepared by diluting 2 ml. of "20 vol." solution to 60 ml. with water; (iii) *standard sulphuric acid*, 0·1 *N*; (iv)

standard salicylic acid: a solution in 10 per cent. alcohol, 1 ml. containing 0·1 mg.; (v) *iron reagent B for colorimetric determination*: a solution of 0·1 g. of anhydrous ferric chloride in 20 ml. of *N* hydrochloric acid diluted to 100 ml. with water; this solution gives a very clear violet tint with salicylic acid and eliminates the possible interference of *p*-hydroxybenzoic acid and other compounds.

EXPERIMENTAL DETAILS.—The benzoic acid is isolated from the sample either by direct extraction with an immiscible solvent or by steam distillation from an acid solution saturated with salt (*cf.* Monier-Williams[3]).* In either case the acid is converted into its ammonium salt by adding dilute ammonia, and the excess of ammonia is removed by boiling in a conical flask until no odour of ammonia is noticed and the vapours are neutral to litmus paper. The solution of ammonium benzoate is then made up to a definite volume.

An aliquot portion of this solution, containing not more than 5 mg. of benzoic acid, is taken for oxidation in a boiling-tube (6 × 1 in.), 5 ml. of 0·1 *N* sulphuric acid is added, and the volume is adjusted to 15 ml. with distilled water; 1 ml. of iron reagent A and 1 ml. of hydrogen peroxide are then added, and the whole is well mixed and heated in a boiling water-bath for 15 minutes *without further shaking*. The solution, which becomes deep violet in colour, is well cooled, about 5 g. of ammonium sulphate are added, and the salicylic acid is extracted with three successive quantities of 15 ml. of ether, each ethereal extract being washed with 5 ml. of water.

The solvent is then completely removed by distillation on a water-bath at 50° C., the residue is dissolved in 50 ml. of 10 per cent. alcohol, 1 ml. of iron solution B is added, and the violet colour produced is compared with the salicylic acid standard made up to 50 ml. with 10 per cent. alcohol.

Under the conditions described 1 mg. of benzoic acid gave approximately 0·1 mg. of salicylic acid, although it should be pointed out that under all the conditions that we have tried a definite gradation was always observed in the proportion of benzoic acid oxidised, according to the amount originally present. This is clearly shown in Table II. It is therefore not strictly permissible to use a fixed ratio in the determination of benzoic acid from the salicylic acid formed. From the results obtained Table III has been constructed, in which the amounts of salicylic acid formed are correlated with the quantities of benzoic acid originally present. This Table, which is an inverse form of Table II, with interpolations, affords a more ready means of converting the quantity of salicylic acid found into terms of benzoic acid.

TABLE II

Benzoic acid taken, mg.	5	4	3	2	1
Salicylic acid found, mg.	0·45	0·41	0·32	0·22	0·13
	0·46	0·42	0·33	0·22	0·13
Benzoic acid converted, per cent.	9·1	10·35	10·55	11·0	13·0

TABLE III

Salicylic acid formed on oxidation, mg.	0·1	0·15	0·2	0·25	0·3	0·35	0·4	0·45
Benzoic acid originally present, mg.	0·77	1·25	1·8	2·3	2·8	3·3	3·85	5·0

* The possibility of the formation of maltol by sugary material in this process must be borne in mind. In this and some other cases a preliminary oxidation with alkaline permanganate, as described later, may be necessary.

The following are a few typical results obtained with some ordinary cordials to which known amounts of benzoic acid were added:

TABLE IV

Sample and quantity taken	Benzoic acid added mg.	Benzoic acid found mg.
Peppermint cordial (50 ml.) ..	17	16·5
Raisin wine (50 ml.)	15	14·2
Orange squash (25 ml.) ..	5	4·9

The method herein described is, in our experience, one of the most sensitive for the *detection* of benzoic acid in food, as 0·5 to 1·0 mg. can be found easily. Moreover, the test is specific; so far as is known, it is given by no other substance, except saccharin,* likely to be present in food.

We have also found the method a rapid and useful one for the *determination* of benzoic acid in food. In a few instances we have compared the results with those obtained by Mohler's test as modified by Illing.[4] This is also a very good test, but unfortunately it is by no means specific for benzoic acid. Also, the accuracy of the method of determination based upon the test depends to a large extent on the stated time being allowed for nitration and strict adherence to other details. The results obtained when the method was strictly followed agreed well with those obtained by Nicholls's method.

PART II. DETERMINATION OF BENZOATES AND SALICYLATES IN PRESENCE OF ONE ANOTHER

The determination of benzoic acid and of salicylic acid in presence of one another is sometimes required, especially in some antiseptic medicines—such as Glycerinum Thymolis Co., B.P.C.—and not infrequently in foreign canned goods.

DETERMINATION OF SALICYLIC ACID.—Of the methods for the determination of salicylic acid in presence of benzoic acid, that of Autenrieth and Beuttel,[5] which consists in precipitating and weighing salicylic acid as tribromophenol bromide, gives good results, but it is somewhat lengthy. The volumetric modification of it (*cf.* B.P. *Assay of Phenol*) is both rapid and accurate for pure salicylic acid, but its use is limited when working on extracts of salicylic acid from food or drugs. We have found that the ferric salicylate test and the Jorissen test, as described below, are satisfactory for determining salicylic acid in presence of benzoic acid.

THE FERRIC SALICYLATE TEST.—In applying this test, if the iron solution B, which is distinctly acid, is used in the colorimetric determination, it will be found sensitive to as little as 0·1 mg. of salicylic acid in 50 ml. in presence of 15 mg. of benzoic acid. In the experiments recorded in Table V, varying amounts of benzoic acid (added as aqueous solution of sodium benzoate), and salicylic acid (added as a solution of the free acid in dilute alcohol) were mixed with 50 ml. of water, 1 ml. of the iron solution B was run in, and the violet colour produced was compared with the salicylic acid standard.

* This substance, if present, should be separated from benzoic acid by extraction of the latter with carbon tetrachloride, in which saccharin is almost insoluble.

TABLE V

Benzoic acid added mg.	Salicylic acid added mg.	Salicylic acid found by ferric salicylate test mg.	Salicylic acid found by Jorissen's test mg.
3	0·1	0·11	0·10
5	0·1	0·10	0·10
10	0·1	0·11	0·10
15	0·1	0·10	0·10
10	0·3	0·29	0·30
15	0·3	0·30	0·31
10	0·4	0·41	0·40
15	0·4	0·41	0·40
10	Nil	No colour	No colour
15	Nil	,, ,,	,, ,,

THE JORISSEN TEST.—Nicholls worked out the best conditions for carrying out this test; these are briefly noted below. It has given excellent results in our hands, and is the most suitable of those available for confirming the presence of salicylic acid and also for its determination in the presence of benzoic acid.

Reagents.—(i) A 2 per cent. solution of sodium nitrite; (ii) a solution containing 0·3 per cent. of crystallised copper sulphate in 10 per cent. acetic acid; (iii) standard colour solution prepared by carrying out the test as described below on 5 ml. of 0·1 per cent. salicylic acid solution diluted to 40 ml., using 5 ml. of each of the reagents (i) and (ii), and diluting the final solution to 100 ml., 1 ml. of this standard colour being therefore equivalent to 0·05 mg. of salicylic acid.

The Test.—To the mixture of benzoic and salicylic acids in about 25 ml. of water are added 1 ml. of each of the reagents (i) and (ii), and the mixture is heated in a boiling water-bath for 15 minutes, cooled, and diluted to 50 ml. The red colour produced is matched by adding the standard colour solution from a burette to a blank consisting of 50 ml. of water containing 1 ml. of reagent (ii).

The degree of accuracy which was attained by this method in our experiments is clearly indicated in Table V.

DETERMINATION OF BENZOIC ACID.—Although it is easy to *distinguish* benzoic from salicylic acid by Mohler's test as modified by Illing (*loc. cit.*),[4] this test cannot be used for the *determination* of benzoic acid when salicylic acid is also present, because the latter also responds, giving a yellow to brownish-yellow colour. We found that Nicholls's method, as modified in the present communication, gives good results if the salicylic acid is first destroyed by alkaline permanganate (*cf.* von der Heide and Jacob).[6]

Preliminary experiments were made upon a solution containing 10 mg. of salicylic acid (as the sodium salt) and 15 mg. of benzoic acid. The salicylic acid was then selectively oxidised by adding 5 ml. of 0·1 *N* potassium hydroxide solution, warming to about 50° C. and adding *N* potassium permanganate solution until a persistent pink colour was observed, about 5 ml. being required. The mixture was acidified with 5 ml. of dilute sulphuric acid (1 in 3), and 10 per cent. oxalic acid solution was added, drop by drop, until a colourless solution was obtained. The benzoic acid was extracted with ether after saturating the solution

with ammonium sulphate, the ethereal extract was washed with water, and the acid was converted into its ammonium salt by two or three shakings with dilute ammonia. The excess ammonia was boiled off, the solution was diluted to 30 ml., and 10 ml. of this (representing 5 mg. of benzoic acid) were taken for the determination as described on p. 175.

The amount of salicylic acid found varied from 0·43 mg. to 0·47 mg. Taking the average, reference to Table III will show that the equivalent of benzoic acid indicated is 5 mg.

The application of these methods to the simultaneous determination of benzoates and salicylates in compound glycerin of thymol, B.P.C., may be quoted as an illustration of their use in a particular case:

Twenty ml. of the sample were diluted to 100 ml., and 20 ml. of this solution were shaken with small quantities of ether to remove the bulk of the volatile oils, etc., and then acidified with dilute sulphuric acid, and the benzoic and salicylic acids were extracted by repeated shakings with ether after partial saturation with ammonium sulphate. The mixed ethereal extracts were washed two or three times with 10-ml. portions of water to remove the colouring matter, the usual precautions to avoid loss of the acids being taken. The acids were then converted into their ammonium salts, and after excess of ammonia had been boiled off, the solution was cooled and diluted to 100 ml. (Solution A).

The salicylic acid was determined in 1 to 2 ml. of this solution by the Jorissen test or colorimetrically as ferric salicylate.

The amount of sodium salicylate found in different samples varied from 0·45 per cent. to 0·52 per cent., the B.P.C. formula requiring 0·52 per cent.

For the determination of benzoic acid 20 ml. of Solution A were taken, the salicylic acid was destroyed by oxidation with alkaline permanganate, and the subsequent oxidation of the residual benzoic acid to salicylic acid and the determination of the latter were carried out as described on p. 176.

The amount of sodium benzoate found in different samples varied from 0·65 per cent. to 0·82 per cent., the B.P.C. formula requiring 0·8 per cent.

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Analytical Laboratories
Royal Dental Hospital
Leicester Square, W.C.2

The Detection and Determination of *p*-Hydroxybenzoic Acid and its Derivatives, with special reference to their Distinction from Salicylic and Benzoic Acids

By F. W. EDWARDS, F.I.C., H. R. NANJI, Ph.D., D.I.C., F.I.C., and M. K. HASSAN, M.Sc.

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The use of *p*-hydroxybenzoic acid,* its sodium salt and its esters, as food preservatives is now quite well known. Of the esters, the commonest are Nipagin A, the ethyl ester; Nipagin M, also known as Solbrol, which is the methyl ester; and Nipasol M, the propyl ester.

Sabalitschka[1] found the propyl ester to be the most effective generally, although the methyl ester was more specifically antiseptic in some cases.

In some foreign countries the use of para-acid and its esters as preservative, either singly or as a mixture, is permitted (*cf.* Analyst, 1934, **59**, 348); they are also used as preservatives for pharmaceutical preparations. In this country the Preservatives Regulations prohibit the use of these compounds, and imported canned goods have frequently to be examined for them. Recently we had reason to suspect the presence of para-acid in imported tins of smoked salmon,[2] and we could find few methods for detecting this acid and its derivatives or for distinguishing them from those of its ortho-isomer, salicylic acid. Although some work had been published (*cf.* Weiss,[3] and Blicke and Smith[4]) the information available on the subject was scanty, and we had to develop methods of detecting para-acid and its esters and of distinguishing them from salicylic and benzoic acids.

Isolation of Salicylic, Benzoic and *p*-Hydroxybenzoic Acids.—Since para-acid may be used in admixture with its esters, the general procedure adopted was to extract these mixed preservatives by means of an organic solvent, such as alcohol or ether, to hydrolyse them with alcoholic potash, and to isolate the acids as their ammonium salts in neutral solution.

The following seven tests were applied to the solutions thus obtained.

I. Test with Millon's Reagent.†—If 20 ml. of the neutral solution of the ammonium salt of para-acid, salicylic acid or benzoic acid, containing the equivalent of as little as 0·1 mg. of the respective acids, is treated with 2 ml. of Millon's reagent and the mixture is heated in a boiling water-bath for two minutes, a red colour is obtained with both salicylic acid and para-acid, whilst benzoic acid gives no colour.

The colours obtained with the two former acids, when compared side by side,

* This acid will usually be referred to as "para-acid" in this communication.

† Millon's reagent gives the best results when prepared as follows:—One part by weight of mercury is dissolved in twice its weight of conc. nitric acid, with gentle warming. The solution obtained is diluted with twice its volume of water. The *freshly prepared* reagent is more sensitive than one that has been kept, and gives a much deeper shade of red.

COPPER *p*-HYDROXYBENZOATE (× 25).

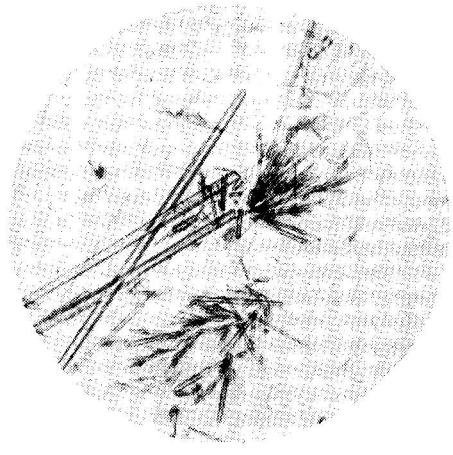

Fig. 1. Slow crystallisation.

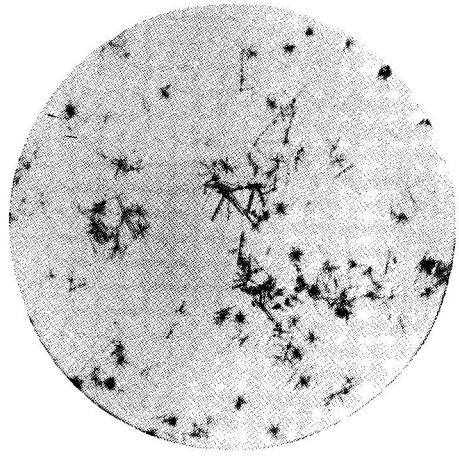

Fig. 2. Rapid crystallisation.

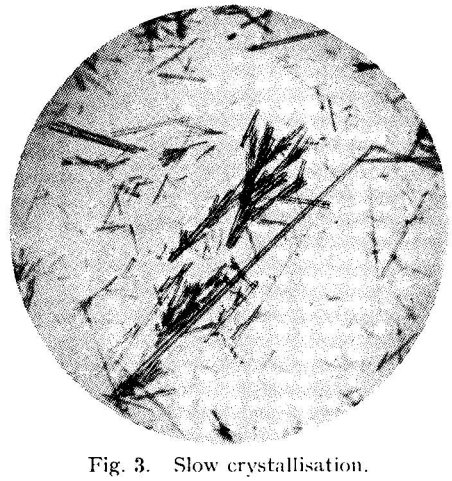

Fig. 3. Slow crystallisation.

are quite distinct, that with para-acid being rose-red and that with salicylic acid being orange-red, but one cannot always rely upon these differences in tint, although they give valuable indications.

This reaction is given by nearly all aromatic substances containing a hydroxyl group attached to the benzene nucleus, and is one of the most sensitive tests for para-acid and salicylic acid in foods; the non-appearance of a red colour within five minutes is a certain proof of the absence of these two acids. If a positive reaction is obtained, confirmatory tests are advisable.

II. FERRIC CHLORIDE TEST.—The contradictory statements published as to the action of ferric chloride solution on para-acid are probably due to the use of different quantities of the acid and different acidities of ferric chloride solution. We obtained the following reactions on adding 1 ml. of the iron reagent B (p. 174) to different quantities of para-acid dissolved in 50 ml. of water:—Five mg., no colour; 10 mg., very slight violet colour; 15 mg., faint violet colour equivalent to that obtained with 0·1 mg. of salicylic acid.

It would therefore appear that salicylic acid is approximately 150 times as sensitive as para-acid in this test when carried out in the manner indicated. Benzoic acid, of course, gives no colour. The possibility that the violet colour is due to traces of salicylic acid present as an impurity in the para-acid has yet to be investigated.

If the Millon test is positive and the ferric chloride test is negative, the absence of salicylic acid is proved, whilst the presence of para-acid is strongly indicated. If, however, the ferric chloride test is also positive, either salicylic acid alone or both acids may be present.

III. JORISSEN'S TEST.—About 10 to 25 ml. of the solution of ammonium salt should be tested exactly as described on p. 176. As little as 0·1 mg. of salicylic acid gives a distinct pink colour. With para-acid under the same conditions 1 mg. gives a very faint yellow colour, and even when the quantity is increased to 10 mg. in 25 ml. of the solution the colour produced is distinctly yellow, not pink. Benzoic acid gives no colour in Jorissen's test. As already stated (p. 176), the test is the most suitable for confirming the presence of salicylic acid. Therefore, a positive Millon test with a negative Jorissen test proves the absence of salicylic acid and raises a strong presumption of the presence of para-acid. Obviously, if the Jorissen test is also positive the presence of salicylic acid is proved, but not necessarily the absence of para-acid.

IV. COPPER-SALT CRYSTALS.—This test depends on the fact that the copper-salt of para-acid is relatively insoluble in water and crystallises out, whereas copper salicylate is very soluble. The appearance of the crystals under the microscope is very distinctive, as will be seen in the photomicrographs (see Plate: Figs. 1, 2 and 3).

The best conditions for this test were achieved by evaporating an aliquot part of the neutral solution of the ammonium salt containing not less than the equivalent of 2 mg. of para-acid (preferably 5 mg.) with 1 ml. of 2 per cent. aqueous copper sulphate solution, on a water-bath to about 1 or 2 ml., and allowing the residue to cool.

In Table I are recorded the results obtained in this test with varying quantities of neutral solutions of para-acid, salicylic acid and mixtures of the two. There

was no difficulty in obtaining the crystals when para-acid alone was present. The presence of copper salicylate definitely increased the time required by the copper *p*-hydroxybenzoate for crystallisation.

TABLE I

Volume of ammonium *p*-hydroxy-benzoate solution (1 ml. = 1 mg. of acid) ml.	Volume of ammonium salicylate solution (1 ml. = 1 mg. of acid) ml.	Results
2	Nil	Crystals in less than 30 minutes
5	,,	,, ,, ,, ,, 15 ,,
10	,,	,, ,, ,, ,, 15 ,,
20	,,	,, ,, ,, ,, 10 ,,
Nil	2	No crystals in 24 hours
,,	5	,, ,, ,, ,, ,,
,,	10	,, ,, ,, ,, ,,
,,	20	,, ,, ,, ,, ,,
2	2	Crystals in 2 hours
2	5	No crystals in 5 hours, but definite crystals in 15 hours
5	5	Crystals within 30 minutes
10	10	,, ,, 30 ,,

This test we consider very important because it is the only one, in our experience, which will definitely prove the presence of para-acid. It should be applied whenever Millon's test is positive. If the characteristic crystals are not formed within 10 or 12 hours the absence of para-acid may be inferred, whereas their formation is a direct proof of its presence, whether or no salicylic acid be also present.

V. NICHOLLS'S TEST.—This test (*cf.* p. 174), like Mohler's test (*infra*), is of use for the detection of benzoic acid in presence of both salicylic and para-acids. If salicylic acid is proved absent by tests II and III, a positive Nicholls test proves the presence of benzoic acid. If salicylic acid is also present, this test should be applied after destruction of the salicylic acid with alkaline permanganate. Alternatively, Mohler's test may be applied without removal of salicylic acid for the mere *detection* of benzoic acid. In *determining* this acid, however, by either Nicholls's test or Mohler's test, salicylic acid must be destroyed; para-acid does not interfere in Nicholls's test.

VI. MOHLER'S TEST.—In applying this test the neutral solution of ammonium salt is evaporated to dryness with 0·1 *N* potassium hydroxide solution in quantity just sufficient to form the potassium salt; the details as described by Illing (*loc. cit.*) are then followed. Benzoic acid gives a red colour, salicylic acid a yellow to brownish-yellow, whilst para-acid gives no colour.

The results of Tests I–VI are summarised in Table II.

It will be noticed that these tests will readily distinguish between salicylic acid and para-acid when they occur separately. Also, it is quite easy, by applying tests II and III to detect and determine salicylic acid in presence of para-acid;

TABLE II

Tests	Para-acid	Salicylic acid	Benzoic acid
I. Millon	Rose-red colour	Orange-red colour	No colour
II. Ferric chloride	No colour (see observations on p. 179)	Violet colour	,, ,,
III. Jorissen	Yellowish colour	Pink colour	,, ,,
IV. Copper crystals	Characteristic crystals	No crystals	——
V. Nicholls (as modified)	No colour	——	Violet colour due to formation of salicylic acid
VI. Mohler (as modified by Illing)	,, ,,	Yellow to brownish-yellow colour	Red colour

but the converse, the detection (and more so the determination) of para-acid in presence of salicylic acid is relatively difficult. In addition to the copper-salt test, a good indirect indication of para-acid in presence of salicylic acid may be obtained as follows:

VII. INDIRECT TEST.—The exact amount of salicylic acid in, say, 20 ml. of the neutral solution of ammonium salts is first determined by test II or III. A fresh 20-ml. portion and a standard containing this amount of salicylic acid in 20 ml. of water are taken for the Millon test. The colours obtained are compared in Nessler glasses after dilution to 50 ml.

In the absence of para-acid the two colours will match well, but if any appreciable quantity of that acid is present the two tints will be different, the test solution being more rose-red than the standard. We have actually made use of this indirect test to determine para-acid in presence of salicylic acid (p. 184).

The scheme shown in Table III will be found useful for the detection of these preservatives when present separately or together in foods, all the tests being carried out on aliquot portions of the neutral solution of the ammonium salts.

TABLE III

Test	Result	Inference	Remarks
I. Millon	No red colour	Salicylic and para-acids absent	Omit tests II, III, and IV
	Red colour	Salicylic and/or para-acid present	Apply tests II, III, and IV
II. Ferric chloride	Violet colour	(*a*) Salicylic acid present	Confirm by test III
		(*b*) Para-acid may also be present	In either case confirm by test IV
	No violet colour	(*a*) Para-acid alone may be present	In either case confirm by test IV
		(*b*) Salicylic acid absent	Omit test III
III. Jorissen	Pink colour	Confirms presence of salicylic acid	
IV. Copper salt	Characteristic crystalline precipitate	Confirms presence of para-acid	
	No crystals within 12 hours	Para-acid absent	
V. Nicholls*	No violet colour	Benzoic acid absent	
	Violet colour	Benzoic acid present	Confirm by test VI
VI. Mohler as modified by Illing	Red colour	Confirms presence of benzoic acid	

* If tests II and III are positive, the preliminary oxidation with alkaline permanganate must be carried out before applying this test.

APPROXIMATE DETERMINATION OF PARA-ACID AND ITS DERIVATIVES IN FOODS

(A) IN ABSENCE OF SALICYLIC ACID.—The rose-red colour produced by para-acid with Millon's reagent is directly proportional to the amount of the acid present and can be utilised for its approximate determination as follows:—Twenty ml. of the neutral solution of the ammonium salt, obtained as described later, containing not more than 2·0 mg. of para-acid,* are treated in a boiling-tube with 2 ml. of Millon's reagent. A series of standards containing 1, 2·5, 5, 7·5, and 10 ml., etc., of an aqueous solution of para-acid (1 ml. = 0·1 mg.) diluted to 20 ml. with water, is prepared in boiling-tubes, and 2 ml. of Millon's reagent are added to each. The test solution and the standards are heated in a boiling water-bath for *exactly* two minutes, and then diluted immediately to 50 ml. in Nessler glasses, and the colours are compared. This determination can be repeated with the quantity of the standard indicated by this preliminary determination so as to obtain a more accurate figure.

Milk.—Ten mg. of the ethyl ester (solution in alcohol) were added to 25 ml. of milk. The milk containing the preservative was treated in a 50-ml. measuring flask, with two 5-ml. portions of phosphotungstic acid reagent,† or 5 ml. of zinc acetate solution,† followed by 5 ml. of potassium ferrocyanide† solution. The mixture was diluted to 50 ml., well shaken, and after about 5 minutes filtered through a dry paper, and 30 ml. of the filtrate were collected. This was saturated with ammonium sulphate and extracted three times with 15-ml. portions of ether, the ethereal extracts being collected in a flask and the ether removed. To the residue 60 ml. of alcohol and 5 ml. of 0·5 *N* alcoholic potash were added, and the mixture was refluxed on a water-bath for two hours. The bulk of the alcohol was then removed by evaporation, and the residue was diluted with water, acidified with dilute sulphuric acid and extracted three times with 15-ml. portions of ether after saturation with ammonium sulphate. The mixed ethereal extracts were shaken three times with 10-ml. portions of 10 per cent. ammonia solution, the mixed ammoniacal extracts were transferred to a conical flask, and the excess ammonia was removed by boiling until the vapours were quite neutral. The neutral solution was cooled and diluted to 100 ml., and 20 ml. were taken for determination with Millon's reagent.

The average recovery of ethyl ester in our experiments with milk was 60 per cent.

Cordials.—Ten mg. of ethyl ester were added to 20 ml. of the cordial. The sample was directly extracted with three successive quantities of 15 ml. of ether after acidifying with dilute sulphuric acid and saturating with ammonium sulphate. After removal of the ether the hydrolysis with alcoholic potash and the conversion of the free acid thus obtained into its ammonium salt were carried out as described under milk, the cooled neutral solution was diluted to 100 ml., and 20 ml. were taken for determination as before.

The recovery of the ester was usually about 90 per cent.

* It was found difficult to obtain a good match when the quantity of para-acid exceeded 2·0 mg.

† These precipitants were prepared exactly as described in the Second Report of the Milk Products Sub-Committee.[5]

In applying the test to alcoholic wines, the alcohol should be removed as far as possible by evaporation before extraction with ether.

Fatty Foods and Meat and Fish Products.—The free acid and its esters are very soluble in alcohol, but only moderately soluble in fats and oils. It was therefore found possible to extract them readily by boiling with successive quantities of alcohol as described hereunder.

Butter.—Ten mg. of the ethyl ester (in solution in alcohol) were thoroughly mixed with 25 g. of the melted butter, and the mixed sample was boiled in a conical flask on the water-bath for thirty minutes with 100 ml. of alcohol, with occasional shaking. The mixture was cooled thoroughly under the tap to let the fat almost solidify and then filtered, and the residue in the flask was washed with two or three successive portions (20 ml.) of boiling alcohol and each time cooled again and filtered. To the mixed alcoholic filtrates 20 ml. of 0·5 *N* alcoholic potash were added, and the subsequent stages of the process were carried out exactly as described for milk. The neutral solution of ammonium salt was diluted to 100 ml., and 20 ml. were taken for the determination.

In working with fatty substances small quantities of free fatty acids are also extracted, and these naturally persist up to the last stage, even making the neutral extract slightly turbid when the excess ammonia is completely removed. These fatty acids, however, are precipitated on addition of Millon's reagent; if they are filtered off, the determination can be continued by heating the filtrate as usual for two minutes and then matching the colours.

The recovery of ethyl ester attained with butter, etc., was usually over 90 per cent.

Sausage.—Ten mg. of the ethyl ester were well mixed with 25 g. of sausage, and the mixed sample was boiled in a conical flask for thirty minutes with 100 ml. of alcohol, with repeated shaking. The mixture was allowed to settle for a minute or two and filtered hot through a Buchner funnel containing a pad of cotton-wool on the top of the filter-paper. The residue in the flask was washed with hot alcohol two or three times and filtered. The alcoholic filtrate obtained was slightly turbid, possibly because of the presence of a little fat or starchy matter which unavoidably filtered through. This did not interfere with the hydrolysis, which was carried out as usual after adding 20 ml. of 0·5 *N* alcoholic potash, and the determination was completed as before. The ammonium salt solution, which was diluted to 100 ml., was again somewhat turbid, as with butter. The same procedure of adding 2 ml. of Millon's reagent to 20 ml., filtering and heating the filtrate in a boiling water-bath, was adopted.

The recovery of ester from sausage and similar foods was found to be of the order of 84 per cent.

The method adopted for sausage is also applicable to minced meat, meat and fish pastes, tinned fish, and similar articles.

The procedure of isolating the preservatives from various foods, as described above, by hydrolysis of the esters is advantageous for two or three reasons. First, para-acid and its esters are often used in admixture with one another, and the identification and determination of the different esters separately through the

particular alcohols produced (*cf.* Weiss[3]) is not only lengthy and tedious, but is also unnecessary, at any rate in food work in this country. It is sufficient to return results as "a preparation of para-hydroxybenzoic acid equivalent to *x* parts of para-hydroxybenzoic acid per million." Secondly, the reaction of the free acid with Millon's reagent is quicker and more delicate than that of the esters, and the red colour is also deeper. Thirdly, the important and decisive copper-salt test can be applied only to the free acid or its neutral salts.

(B) IN PRESENCE OF SALICYLIC ACID.—The exact determination of the amount of para-acid in presence of salicylic acid is a matter of some difficulty. We attempted to separate the two quantitatively through their copper-salts, using different solvents, such as 50 per cent. alcohol, acetone, etc., but without success.

In the preliminary experiments we observed that with Millon's reagent the two acids give a reddish colour of equal depth, but of different shades, and that a good estimate of the proportion of the one to the other could be arrived at by comparing with a series of mixed standards as follows:

The exact amount of salicylic acid is first determined in the neutral extract of the mixed ammonium salts by tests II or III. The volume of this solution is then adjusted to contain 0·5 mg. of salicylic acid in 20 ml., this volume being taken for the Millon test. A series of mixed standards is prepared in which the proportions of salicylic acid (the amount of which is kept constant) to para-acid in the 20 ml. are 0·5 : 0·1, 0·5 : 0·25, 0·5 : 0·5, 0·5 : 0·75, 0·5 : 1·0, and so on, all in mg. in 20 ml. It is, of course, not essential to adjust the concentration to contain 0·5 mg. of salicylic acid in 20 ml. of the neutral solution of the mixed ammonium salts so long as this concentration is not exceeded. This is merely a convenient dilution, and any weaker one may be chosen, but it is essential that the exact quantity of salicylic acid be known. If, for instance, the dilution is such that 20 ml. contains only 0·2 mg. of salicylic acid, all the mixed standards should be made to contain this amount of salicylic acid, whilst the quantities of para-acid are varied as above.

The tests are completed as described, and it will usually be found possible to estimate the relative proportions with a fair degree of accuracy.

The method is illustrated by the following experiments. A cordial containing 0·025 per cent. of salicylic acid and 0·025 per cent. of para-acid was prepared. The mixed acids were isolated as usual as their ammonium salts, and this solution was diluted to 1000 ml., so that 20 ml. taken for the test contained 0·5 mg. of salicylic acid. Mixed standards were prepared in which the proportions of salicylic acid to para-acid were (*a*) 0·5 : 0·3, (*b*) 0·5 : 0·4, (*c*) 0·5 : 0·5, (*d*) 0·5 : 0·6, and (*e*) 0·5 : 0·7 —all in mg. in 20 ml. The tests were completed as usual. The colour obtained with the test solution was markedly different from those in standards (*a*), (*d*) and (*e*), but it was a little difficult to decide whether it matched (*b*) more closely than (*c*), thus indicating that the proportions were almost equal.

In certifying adulteration when indications are obtained that both these acids are present together, it is perhaps advisable to return the results as "a preparation of hydroxybenzoic acid equivalent to *x* parts of hydroxybenzoic acid per million" without giving the proportions of the two isomers found.

We are indebted to Mr. J. R. Nicholls, of the Government Laboratory, for some useful suggestions and for his valued criticism. We also wish to thank

Mr. E. B. Parkes, of the Bristol Police Laboratory, for kindly preparing the photomicrographs.

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ANALYTICAL LABORATORIES
ROYAL DENTAL HOSPITAL
LEICESTER SQUARE, W.C.2

The Use of Hexamine for the Separation of Thorium from the Rare Earths, and its application to the Determination of Thorium in Monazite Sand

BY A. M. ISMAIL, PH.D., AND H. F. HARWOOD, M.SC., PH.D., F.I.C.

HEXAMINE (hexamethylenetetramine) has been used by various workers as a precipitant for certain metallic radicles; it was employed by Kollo[1] in the separation of iron from manganese, and Kollo and Georgian[2] extended its use to the separation of aluminium from calcium, recommending it in place of ammonia. They explained the mechanism of the reaction which takes place when hexamine is used as a precipitant, pointing out that it decomposes when boiled with the salt solution, ammonia being formed.

Rây and Chattopadhya[3] described hexamine as a reagent which effects a quantitative separation of ferric iron from zinc, cobalt, nickel and manganese. They gave a thorough and clear explanation of the reaction involved, and showed also that this reagent will precipitate aluminium, titanium and thorium. Rây[4] extended the application of hexamine as an analytical reagent to the determination of the metals of the ammonium hydroxide group in the presence of manganese, nickel, cobalt and magnesium. Hexamine precipitates quantitatively the hydroxides of ferric iron, aluminium, chromium, titanium, uranium, zirconium and thorium, but in the presence of ammonium salts, zinc, manganese, nickel, cobalt and magnesium remain in solution. The method given permits of the quantitative separation of iron from all the last-mentioned bivalent metals; aluminium is readily separated from all except nickel, although the separation from large quantities of zinc is incomplete. The separation of titanium is quantitative except when large amounts of zinc are present, and the separation of uranium presents no difficulties. A separation of zirconium and thorium from the bivalent metals of the ammonium sulphide group can also be effected by hexamine.

Rây examined the behaviour of hexamine towards solutions of the salts of the rare earths. Lanthanum, cerium, praseodymium, neodymium, and yttrium gave no precipitate in the cold, but on heating the solution to boiling a faint turbidity formed; the addition of ammonium salts completely prevented this. No separation of the rare earths from manganese, cobalt, nickel and zinc could be effected with hexamine, neither did Rây examine the possibility of a separation of thorium from the rare earths with this reagent.

THE HEXAMINE METHOD FOR THE SEPARATION OF THORIUM FROM THE RARE EARTHS.—The following table (due to Britton[5]) gives the hydrogen ion concentrations at which certain hydroxides are precipitated.

	*p*H		*p*H
Magnesium ..	10·5	Lead	6·0
Silver	9 (?)	Beryllium	5·7
Manganese	8·5–8·8	Iron (ous)	5·5
Lanthanum ..	8·4	Copper (ic)	5·3
Cerium (ous) ..	7·4	Chromium	5·3
Mercuric	7·3	Zinc	5·2
Praseodymium ..	7·1	Uranium	4·2
Neodymium ..	7·0	Aluminium ..	4·1
Samarium	6·8	Thorium	3·5
Cobalt	6·8	Tin (ous)	2 (?)
Yttrium	6·8	Zirconium	2 (?)
Cadmium	6·7	Iron (ic)	2 (?)
Nickel	6·7		

The great difference in the hydrogen ion concentrations accounts for the ease with which thorium can be separated from the rare earths by methods depending on the change in *p*H. Reagents which have been used for controlling the hydrogen ion concentration in such a separation are sodium thiosulphate and sodium azide; a separation can also be effected by hexamine. This latter substance is an exceedingly weak base, and its aqueous solution has a neutral reaction to litmus. In the presence of hydrogen ions it is hydrolysed into formaldehyde and ammonia, the hydrogen ions formed through the hydrolysis of salts already in the solution being frequently enough for the decomposition of the hexamine to proceed. The hydrolysis of thorium salts in solution is sufficiently great to cause the precipitation of thorium hydroxide on the addition of hexamine, even in the presence of ammonium salts which lower the hydroxyl ion concentration of the ammonium hydroxide produced from the hexamine. On the other hand, the precipitation of the hydroxides of cerium, lanthanum, yttrium, etc., by hexamine is completely prevented by the presence of ammonium salts, even if the solution is heated to boiling.

The following Tables, A to F, give the results obtained in the course of investigations made to ascertain the best conditions for separating thorium from cerium (and the other rare earths) by means of hexamine. The thorium and cerium nitrates used in these experiments were of a high grade of purity. Stock solutions of the two salts were prepared, and standardised carefully by precipitation with (*a*) oxalic acid, and (*b*) ammonia.

The salts of lanthanum, praseodymium, neodymium, and yttrium used in some of the experiments were also the purest obtainable nitrates that could be purchased.

In the course of the actual determinations the precipitates of thorium hydroxide obtained in the separation were ignited directly to oxide, and the cerium in the filtrate was precipitated by the addition of ammonia (together with a few drops of hydrogen peroxide when lanthanum was present), the precipitate being ignited and weighed as the oxide.

Separation of Thorium from Cerium

Table A

Weight of ammonium chloride added, 5 g.
Volume of solution 100 ml.
Temperature 30°.
The precipitant (hexamine) was added rapidly, and only a single precipitation was made.

ThO_2 used g.	CeO_2 used g.	CeO_2 found g.	Difference	ThO_2 found g.	Difference g.
0·0420	0·0370	0·0371	+0·0001	0·0419	−0·0001
0·0420	0·0370	0·0365	−0·0005	0·0420	Nil
0·0420	0·0185	n.d.	—	0·0421	+0·0001
0·0420	0·0093	0·0090	−0·0003	0·0424	+0·0004
0·0420	0·0047	0·0045	−0·0002	0·0420	Nil
0·0210	0·0370	0·0369	−0·0001	0·0212	+0·0002
0·0105	0·0370	0·0367	−0·0003	0·0109	+0·0004
0·0027	0·0370	0·0352	−0·0018	0·0038	+0·0011
0·0027	0·0370	0·0362	−0·0008	0·0035	+0·0008

Table B

Weight of ammonium chloride added, 5 g.
Volume of solution 100 ml.
Temperature 30°.
The precipitant was added, drop by drop, with continual stirring of the solution, and only a single precipitation was made.

ThO_2 used g.	CeO_2 used g.	CeO_2 found g.	Difference	ThO_2 found g.	Difference g.
0·0076	0·0370	0·0362	−0·0008	0·0085	+0·0009
0·0076	0·0370	n.d.	—	0·0077	+0·0001
0·0050	0·0370	0·0361	−0·0009	0·0064	+0·0014
0·0050	0·0370	n.d.	—	0·0055	+0·0005
0·0027	0·0370	0·0362	−0·0008	0·0036	+0·0009
0·0027	0·0370	0·0367	−0·0003	0·0037	+0·0010

The results in Tables A and B show a slight positive error in the figure for the thoria, more especially when the amount of cerium present is greatly in excess of that of the thorium. A further set of determinations was then carried out in which the thorium precipitate first obtained was re-dissolved, and the precipitation with hexamine was repeated. As is evident from the figures in Table C, this procedure effects a perfectly satisfactory separation, even when a very large excess of cerium is present.

TABLE C

Conditions as in B, except that a double precipitation of the thorium was made.

ThO_2 used g.	CeO_2 used g.	CeO_2 found g.	Difference	ThO_2 found g.	Difference g.
0·0076	0·0370	0·0370	Nil	0·0076	Nil
0·0050	0·0370	0·0369	−0·0001	0·0050	Nil
0·0027	0·0370	0·0368	−0·0002	0·0026	−0·0001

SEPARATION OF THORIUM FROM LANTHANUM, NEODYMIUM, PRASEODYMIUM, AND YTTRIUM

TABLE D

Conditions as in C.

ThO_2 used g	Rare earth oxides used, g	ThO_2 found g.	Difference g.
0·0420	0·242 Ce, La, Nd, Pr, Y	0·0427	+0·0007
0·0420	0·242 ,, ,,	0·0426	+0·0006
0·0420	0·040 La oxide	0·0421	+0·0001
0·0420	0·040 Pr oxide	0·0421	+0·0001
0·0420	0·040 Nd oxide	0·0422	+0·0002
0·0420	0·040 Y oxide	0·0424	+0·0004

TABLE E

Conditions as in D, except that after a double precipitation of the thorium with hexamine, the hydroxide was re-dissolved, and the thoria was precipitated as oxalate, ignited and weighed.

ThO_2 used g.	Rare earth oxides used, g.	ThO_2 found g.	Difference g.
0·0420	0·040 Y oxide	0·0420	Nil
0·0420	0·040 Nd oxide	0·0419	−0·0001
0·0420	0·242 Ce, La, Nd, Pr, Y oxides	0·0420	Nil
0·0420	0·242 ,, ,,	0·0420	Nil

In the two following determinations the thorium and rare earths were first precipitated with oxalic acid, the oxalates were ignited, the oxides were dissolved in hydrochloric acid, and the thorium was separated as before by a double precipitation with hexamine, ignited to oxide and weighed.

ThO_2 used g.	Rare earth oxides used, g.	ThO_2 found g.	Difference g.
0·0420	0·242 Ce, La, Nd, Pr, Y	0·0421	+0·0001
0·0420	0·242 ,, ,,	0·0420	Nil

The method finally adopted for the precipitation of thorium by hexamine in the presence of cerium and other rare earths is as follows:—The faintly acid solution of the metals, which should have a volume of 100 ml., is warmed to 30° C., and 5 g. of ammonium chloride are added. A 10 per cent. solution of hexamine is then added, drop by drop, with stirring after each addition, until a slight excess is present. The precipitate of thorium hydroxide is allowed to settle, the liquid is decanted through a Whatman No. 41 filter, and the precipitate is finally transferred to the paper and washed with warm 2 per cent. ammonium nitrate solution. The

precipitate is then dissolved on the filter with hot 2 *N* hydrochloric acid, and the paper is well washed with hot water. The solution is diluted if necessary, neutralised with ammonia, and made faintly acid to methyl red with hydrochloric acid. Sufficient ammonium chloride is then added to bring its content in the solution up to 5 per cent., the solution is warmed, and the thorium is precipitated as before. The washed precipitate is ignited and weighed as ThO_2.

The cerium in the united filtrates is precipitated by the addition of a slight excess of ammonia and a few drops of 6 per cent. hydrogen peroxide to the hot solution, the liquid being then boiled for 2 minutes, and the precipitate of cerium hydroxide filtered off, washed with hot 2 per cent. ammonium nitrate solution, ignited and weighed.

In the majority of cases a single precipitation of the thorium suffices to give a satisfactory separation, but if the greatest accuracy is required, and especially if the amount of cerium present preponderates greatly over the thorium, a double precipitation, as described above, is advisable.

APPLICATION OF THE METHOD TO THE DETERMINATION OF THORIA IN MONAZITE SAND.—Five g. of the sand, ground to a fine powder, are weighed into a platinum dish, and sulphuric acid (about 25 ml.) is added so as to produce a stiffish paste. The dish is then covered and heated at 150–180° C. for four hours, with frequent stirring. After cooling, the contents of the dish are added to about 180 ml. of water at 0° C., in small portions at a time, and with constant stirring. The beaker is kept immersed in ice-water to maintain the temperature at 0° C. during solution. The pasty mass dissolves completely, with the exception of a small residue composed chiefly of zirconium and silicon compounds. The dish is then well rinsed out with cold water, and the whole is well mixed and allowed to stand for some hours, or preferably overnight. The solution is filtered into a 250-ml. graduated flask, the residue and filter are well washed with cold water acidified with sulphuric acid, and the solution is diluted to the mark and well mixed. Fifty ml., representing 1 g. of the original sand, are pipetted into a 150-ml. beaker and nearly neutralised with ammonia, concentrated ammonia being used at first, and a dilute solution towards the end of the neutralisation; 1·5 ml. of conc. hydrochloric acid are quickly added, the solution is diluted to 70 ml. and heated to 60° C., and then 30 ml. of a cold, saturated solution of oxalic acid are added, drop by drop, with vigorous stirring. The whole is kept at 60° C. for one hour, then well stirred and allowed to stand overnight. The liquid is decanted through a Whatman No. 40 filter, and the precipitate is transferred to the paper and washed with a warm solution containing 2 per cent. of oxalic acid and 0·1 per cent. of hydrochloric acid; the oxalates are then ignited to convert them into oxides.

The ignited oxides are transferred to a beaker, and the crucible is rinsed well with dilute (1 : 1) hydrochloric acid. Ten ml. of this acid are poured into the crucible, which is then heated on a water-bath to dissolve any traces of oxide adhering to the walls. The resulting solution is added to that already in the beaker, and more acid is introduced until the total volume of liquid is about 50 ml.; finally, 10 drops of 6 per cent. hydrogen peroxide are added. The covered beaker is heated with a small flame, so that the liquid is kept just below the boiling-point. Complete solution of the oxides is attained after about two hours.

The clear solution of the chlorides is evaporated to dryness, 1·5 ml. of hydrochloric acid are added, the residue is taken up with water, and the solution is diluted to 50 ml. The whole is heated to 60° C., and the rare earths are again precipitated by the addition of 25 ml. of oxalic acid solution. The precipitate is filtered off, washed, ignited and weighed. It is then dissolved in hydrochloric acid as before, the solution is again evaporated to dryness, and the residue is moistened with two drops of hydrochloric acid. Water is then added, and the solution is diluted to 100 ml.; the thorium present can then be separated and determined by the hexamine method previously described.*

The following table shows the results obtained in the analysis of a number of samples of monazite sand† by the hexamine method. As a check, the thorium content of three of the samples was also determined by the standard thiosulphate method. As will be seen from the table, the agreement between the two sets of figures obtained is perfectly satisfactory. The separation of thorium from the rare earths by the thiosulphate method, although yielding good results, is tedious and requires considerable time. Re-precipitation of the thoria more than once is necessary, in order to effect a complete separation, whilst, on the other hand, the filtrates obtained in the process must all be worked up to recover the traces of thoria which they contain, with considerable expenditure of time. A further drawback is the separation of sulphur during the boiling of the solution with sodium thiosulphate, and the consequent impossibility of telling whether any precipitation of thoria has taken place, especially when small amounts of this element are in question.

The hexamine method gives a sharp separation of the thoria after two precipitations with the reagent, and effects a considerable saving of time, as the precipitate of thorium hydroxide is readily filtered off and washed, and no reworking of the filtrates is necessary, as in the thiosulphate method.

DETERMINATION OF THORIUM IN MONAZITE SAND

Sample	Hexamine method Thorium dioxide, per cent.	Thiosulphate method Thorium dioxide, per cent.
1	7·32	7·30
	7·40	7·38
2	7·85	7·83
	—	7·89
3	9·10	—
	9·20	—
4	10·04	—
	10·08	—
	10·07	—
5	9·76	9·83
	9·77	9·78

* In order to ensure complete precipitation of the rare earth oxalates the amount of rare earth oxides present in 100 ml. of solution should not be less than 1 g.

The sulphuric acid solution of the sand should be carefully neutralised by adding the dilute ammonia, drop by drop, stopping the addition before a faint permanent turbidity is produced; the hydrochloric acid is then quickly added. The solution should be clear, and remain so when heated to 60° C. If the neutralisation is carried out as described, a second oxalate precipitation of the rare earths will frequently prove unnecessary.

† Most of the samples used were kindly furnished by Mr. S. J. Johnstone, of the Imperial Institute, and Mr. H. F. V. Little, of Thorium, Ltd., to whom we wish to express our thanks.

SUMMARY.—Thorium can be quantitatively separated from cerium and other rare earths by using hexamine as a precipitant. The application of the method to the determination of thorium dioxide in monazite sand is described.

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IMPERIAL COLLEGE OF SCIENCE
AND TECHNOLOGY
SOUTH KENSINGTON, S.W.7

Notes

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

THE DETERMINATION OF ANTIMONY IN LEAD-RICH ALLOYS

HAVING frequent occasion to determine antimony in lead-rich alloys for the purpose of works control, I read with much interest the paper by K. Stanford and D. C. M. Adamson in the January ANALYST.

The method employed here is a modification of that described by Low in his textbook (*Technical Methods of Ore Analysis*, 1927, p. 296).

A one-gram sample in a 500 ml. Pyrex conical flask is digested with 10 ml. of conc. sulphuric acid, to which is added about 5 g. of anhydrous sodium sulphate. The flask is held in Fisher tongs over the flame of a large Bunsen burner, and a few minutes' vigorous boiling suffices to produce an almost white melt. When cool, this is gently warmed with 30 ml. of water and 20 ml. of hydrochloric acid until the sodium salts are in solution, when the contents are briskly boiled for 30 seconds. Eighty ml. of water are then added, the flask is cooled to below 20° C., and the solution is titrated in the usual way with permanganate solution which is equivalent to approximately 0·01 g. of antimony per ml.

The advantages of a conical flask over a crucible for the attack are obvious, especially when many samples have to be analysed, and anhydrous sodium sulphate is an innocuous reagent which is more conveniently handled than the bisulphate.

No trouble is met with from adsorption of antimony, but, under these conditions, the titration is not strictly proportional in presence of lead, slightly more permanganate being required than for the same weight of antimony alone. Tables I and II, in the paper under discussion, support this observation by showing a tendency towards a negative error in the absence, and a positive error in the presence, of lead.

In my experience, the magnitude of the error is dependent upon the relative proportions of antimony and lead present. Presumably lead, by virtue of the fact that the final solution is saturated, may be regarded as constant in amount when it is the major constituent. The error, which may amount to 0·10 ml. or 0·1 per cent. on an alloy containing 10 per cent. of antimony, may be made negligible by standardisation with similar proportions and amounts of the two metals.

R. G. ROBINSON

BRITANNIA LEAD CO., LTD.
NORTHFLEET, KENT

THE DEVELOPMENT OF LATENT FINGER-PRINTS WITH DYESTUFFS

In the course of his lecture to the Manchester Section of the Institute of Chemistry, on January 14th, Dr. Ainsworth Mitchell mentioned that he had used various dyes, notably methylene blue, for the development of latent finger-prints on documents, but that the method had the drawback that the developed prints were readily smudged.

As a result of the discussion on this point, I have made a number of experiments with basic dyestuffs and find that Victoria Blue BS is satisfactory for the purpose. In these experiments the cleaned fingers, thumbs and, in one instance, the whole hand, were pressed on to white cardboard, and the basic dyestuff in powder form was dusted over the cardboard. Basic dyestuffs have the property of being readily absorbed by grease, and therefore clearly showed up the ridges where grease had been transferred from the fingers and thumb on to the card. In order to fix the dyestuff, the cards were held for a few minutes over boiling 30 per cent. aqueous acetic acid solution, the fixation being effected by acetic acid vapour and steam. In this way positives are obtained, and should be suitable for photographing. The finger-prints on the cards thus obtained should also be quite durable if kept in the dark. Basic dyestuffs, however, are rather fugitive to light.

H. A. Thomas

Imperial Chemical Industries, Ltd.
(Dyestuffs Group)
Hexagon House
Blackley, Manchester

OPTICAL ACTIVITY OF PREPARATIONS OF SQUILLS

Of several samples of Acetum Scillae and Tinct. Scillae examined in this Laboratory, all have been found to possess a marked degree of optical activity (laevo-rotatory).

These observations were made during an investigation carried out to determine the reason why samples of Oxymel Scillae B.P., 1932, failed repeatedly to pass the test for optical rotation, invariably giving a reading in excess of the B.P. limit of $-1{\cdot}9$ for a 25 per cent. w/v solution.

It would appear that the B.P. limits for the optical rotation of Oxymel Scillae had been drawn up on the assumption that only the honey present contributed to the optical activity of the preparation.

It seems necessary, in the light of the foregoing observations, that the optical activity of the Acetum Scillae used in making Oxymel Scillae should also be taken into account in calculating the official limits for optical rotation, and that the limiting figure should be considerably higher on the laevo side than at present.

Leo McGraghan

Analytical Laboratory
Messrs. Brady & Martin, Ltd.
Newcastle upon Tyne

Official Appointments

THE Minister of Health has approved the following appointments:

REGINALD FRANK WRIGHT as a Public Analyst for the County Borough of Eastbourne, in addition to S. Allinson Woodhead (November 10th, 1936).

REGINALD FRANK WRIGHT as a Public Analyst for the Borough of Hove, in addition to S. Allinson Woodhead (November 26th, 1936).

ARTHUR EDGCOME BROWN as additional Public Analyst for the Metropolitan Borough of Deptford from January 1st, 1937, in addition to Hugh Amphlett Williams, who becomes Senior Public Analyst from April 1st, 1937. H. G. Harrison retired March 31st, 1937 (January 6th, 1937).

ERIC VOELCKER as a Public Analyst for the Borough of Chipping Wycombe in place of B. H. Gerrans (deceased) (January 6th, 1937).

HUGH AMPHLETT WILLIAMS as Additional Public Analyst for the Metropolitan Borough of Greenwich, in addition to A. E. Brown (January 6th, 1937).

Department of Scientific and Industrial Research

FOOD INVESTIGATION. Special Report No. 44

SECOND REPORT ON THE CORROSION OF THE TIN-PLATE CONTAINERS BY FOOD PRODUCTS*

IN the First Report on this subject (*cf.* ANALYST, 1931, **56**, 315) the methods of preventing or mitigating the corrosion of tin-plate containers were discussed. Since then considerable advances have been made in lacquers and methods of applying them. The drawback of the custom of lacquering the flat sheet and fashioning and soldering the bodies after stoving is that some damage to the can is bound to occur. To remedy this, attempts have been made in U.S.A. to spray finished cans with a further coating of lacquer of a type that would require only a short stoving. If satisfactory synthetic lacquers can be developed that need stoving for only 10 or 20 minutes, or even less, it may become possible to abolish lacquering on the flat.

ALTERNATIVES TO TIN-PLATE.—Glass now used is highly resistant to blows and changes of temperature, and rapid mechanical handling, filling and hermetic sealing with metal caps may reduce the cost almost to that of tin-plate.

Aluminium.—The use of aluminium cans for fish products is increasing, especially in Norway. Aluminium does not blacken when used with crustacea, etc., nor bring about in fish products those slow changes (darkening, etc.) that have been associated with traces of iron derived from the can. Aluminium cans have not, so far, proved successful with tomato, fruits, etc., owing to the rapid formation of hydrogen-swells. Moreover, aluminium plate is not so strong as tin-plate and is more difficult to make into cans, so that it is unlikely to come into general use.

THE CORROSION OF TIN.—Except for special purposes, the general methods of research and the apparatus previously used have been little modified. As before, citric acid (0·5 to 1 per cent.) has for the most part been used as the basal corroding medium, with sodium citrate as a buffer to give a *p*H-range from about 2·4 to 5·5.

Specimens of steel and tin for the immersion tests have been prepared by

* By T. N. Morris, M.A., and J. M. Bryan, B.Sc., Ph.D. London: H.M. Stationery Office. Price 1s. net.

treatment with emery cloth and by degreasing with benzene and other solvents. Specimens of tin-plate have also been treated with emery to remove a definite area of the tin, thus forming a convenient tin-iron couple for immersion tests, the technique being as follows:—The specimen is first degreased, and the portion to be left intact is coated with paraffin wax. The portion to be de-tinned is then immersed in Clarke's reagent (ANALYST, 1934, **59**, 525) until one minute after the evolution of gas has ceased. All the tin is thus removed, together with the greater part of the tin present in the tin-iron compound. The wax is then dissolved off, and the specimen is clamped in a frame that protects the tinned portion, while the bare portion is treated with emery to obtain the standard surface.

Effect of Ferrous Iron.—Experiments in which the *p*H was varied or kept constant showed that the concentration of stannous tin is at a maximum at *p*H 3, whilst stannic tin predominates at *p*H 4 to 5·5. In other words, during the early stages of corrosion oxygen is more efficient quantitatively as a corroding agent for tin in the presence of ferrous iron at *p*H 3 than at any other point on the range. Increasing the concentration of iron in solution considerably increased the quantitative efficiency of oxygen as a corroding agent in the early stages of the test.

Effect of a Stannic Salt.—The presence of small quantities of a stannic salt had no apparent effect on the corrosion of tin over the range *p*H 2·4 to 5·5; hence a stannous salt would not act catalytically in promoting the corrosion of tin in presence of oxygen by alternate oxidation and reduction.

Effect of Copper.—Quantities of copper, up to 20 p.p.m. as citrate, were substituted for ferrous iron in the experiments. The results showed that the copper ion is not as effective as iron in accelerating the corrosion of tin in presence of air.

Sucrose.—Experience has shown that fruits packed in water give rise to fewer hydrogen-swells than fruits packed in syrup. It has been suggested that the explanation may be found in the presence of sulphur in the sugars used. In the experiments described the presence of sugar inhibited corrosion at 25° C. over the whole *p*H range, reducing it to one-third of the normal at *p*H 2·4, and to one-half at *p*H 5·5. Increasing quantities of sugar in the presence of 0·5 per cent. of citric acid at 25° C. progressively retarded the rate of corrosion of tin, probably owing to the progressive reduction of the solubility of air in the solutions. At 75° C. corrosion was stimulated, but this might have been due to products of the breakdown of the sugar, since considerable caramelisation occurred.

Sodium Chloride.—At 25° C. 1 per cent. of salt in presence of 0·5 per cent. of citric acid had no effect at *p*H 2·4, but from this point up to *p*H 5·5 there was a slight inhibiting effect on corrosion. At 75° C., with solutions containing 1 per cent. of citric acid, not buffered, and 2 per cent. of sodium chloride, the salt had an inhibiting effect.

Acids other than Citric Acid.—The hydroxy acids, lactic, tartaric and malic, had about the same corrosive powers as citric acid, but tin was not attacked by the non-hydroxy acids, acetic and succinic. This difference in behaviour towards tin finds a parallel in the behaviour of the respective sodium salts towards aluminium. Oxalic acid has strong corrosive powers, the metal becoming coated with an insoluble layer, probably tin oxalate. Phosphoric acid has little action; sulphuric acid proved less corrosive, and hydrochloric acid more corrosive than the hydroxy organic acids.

THE CORROSION OF MILD STEEL.—It has been suggested that the differences often found in the rate at which different specimens of steel and iron corrode under the same conditions may be due to variations in the amount of phosphorus in the steel; it is, however, quite as likely that sulphur in the steel is responsible; evidence in support of this is put forward in the Report.

The quality of steel must be considered in relation to the rate of diffusion of hydrogen through it, as well as to the velocity of corrosion. The formation of

blisters is considered to be due to hydrogen assuming the gaseous form as inclusions or cavities in the steel. There is evidence that cold-rolling the steel sheet influences the rate of corrosion and results in a decreased tendency to the formation of hydrogen-swells; any factor improving the continuity of the tin coating will probably also improve that of the lacquer.

The Report also discusses the action of inhibitors and accelerators on the corrosion of mild steel, and experiments (described in detail) have been carried out on the corrosive action of various fruit juices.

Effect of Beet Sugar.—Commercial beet sugars commonly have an inhibiting effect on the corrosion of iron, and the favourable influence of adding a brown beet sugar to pure white sugar has been demonstrated in actual canning tests.

SULPHUR COMPOUNDS.—The effect of either sulphur dioxide or hydrogen sulphide in canning fruits of high acidity is to hasten the formation of hydrogen-swells.

THE TIN-IRON COUPLE AND TIN-PLATE.—In much of the work strips of tin-plate were adapted for a study of the tin-iron couple by laying bare definite proportions of the underlying steel. The following conclusions were drawn:

(i) In the absence of air, no matter what the relative areas of iron and tin may be, the corrosion of tin increases from *p*H 2 to *p*H 4, and sometimes beyond, while the corrosion of iron diminishes.
(ii) The presence of air increases the corrosion of tin, especially at high acidity.
(iii) Unless a very large proportion of tin is exposed, the corrosion of iron tends to be lower in the presence than in the absence of air, particularly at high acidity.

DISCOLORATION OF CANNED FRUITS.—Amounts up to 40 p.p.m. of aluminium, copper, nickel, chromium, zinc, lead and silver had no effect on the colour of fruits at room temperature or at 70° C. Strawberries are particularly sensitive to iron, 2 p.p.m. producing marked discoloration. With black currants, the greatest discoloration was produced by tin and the least by iron. Raspberries were only slightly discoloured by 10 p.p.m. of tin. The reason for the different behaviour of iron and tin lies in the fact that iron affects the tannins and allied substances derived from the seed-coats of the fruits, whilst tin affects the soluble anthocyanin pigments.

Queensland

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDED JUNE, 1936

THE Acting Government Analyst (Mr. Frank E. Connah) reports that 13,656 samples were examined, as compared with 12,550 for the previous year. Of these, 6568 were for the Health Department, 2059 for the Customs and 345 for the Police. Among the points of interest to which special attention is directed are the following:

DIRT IN MILK.—The position with regard to visible dirt is fairly satisfactory. Very rarely does the weight of dirt in a sample exceed 1 grain per gall., but in sound dairy practice there should not be more than one-third of a grain. Under the pressure of modern dairy hygiene the old tolerance of 1·5 grain of visible dirt per gall. must be buried with an unclean past.

FORMALDEHYDE IN CURED FISH.—The Torry Research Station recorded some high formaldehyde results (about 10 p.p.m.) by Schryver's test on dry salt ling to which no formaldehyde had been added (ANALYST, 1936, **61**, 340). Our experiments on tailer and mullet fish did not afford any evidence by this method of the

presence of formaldehyde either in the fresh or salt-cured fish. Our reports on formaldehyde in fish have not been invalidated by the Torry Station investigation. Of 15 samples of cured fish examined, 14 contained formaldehyde in amounts ranging from 24 to 510 p.p.m. In some instances the odour of formaldehyde was pronounced. With imported moist lightly salted filleted haddock, only 4 p.p.m. was recorded.

LEAD IN PAINTS, CRAYONS AND TOYS.—Of 67 samples of paint examined, 45 contained more than 5 per cent. of soluble lead. Under the Queensland Health Acts no paint pigment may contain more than 5 per cent. of soluble lead, and soluble lead is determined, as in England,* by the method of Thorpe and Simmonds (*J. Chem. Soc.*, 1901, **79**, 792). Large differences in the soluble lead-content of commercial chrome paints were found.

Of 324 samples of crayons submitted, 112 contained lead compounds, and 6 of these also contained arsenic. The lead ranged from 0·7 per cent. to 31 per cent., and the arsenic from 0·2 per cent. to 1·7 per cent. The sample containing the highest proportion of arsenic was coloured with London Purple, a by-product in the manufacture of dyes. London Purple contains a high proportion of calcium arsenite and is used as an insecticide. Thirty per cent. of the lead contained in some of the "chalk" crayons was soluble in the solvent prescribed for the determination of soluble lead in paint.

Only 3 of 38 samples of toys examined were free from lead. Four toy motor cars and one bugle were made of an alloy containing 86 per cent. of lead and 14 per cent. of antimony.

BLACK LIVER IN SHEEP.—Sheep livers and kidneys were examined for the purpose of determining the cause of black liver in sheep. The black livers, which were uniformly black and unsaleable as human food, represented only a very small proportion of the total livers. The health of sheep does not appear to be affected in any way through black liver. The following table gives

Colour of liver	Parts per million (on wet substance)			
	Copper	Iron	Calcium	Sulphur
Black	152	117	162	3,000
Black	263	77	117	2,900
Black	154	90	57	2,884
Black	152	121	75	—
Black (mottled)..	125	156	920	—
Normal	24	46	81	2,500
Normal	10	76	93	2,800
Normal	4	176	156	—
Normal	42	150	106	—

Although the black livers contained more copper than normal livers, it has not been demonstrated that the blackening is due to the higher copper-content.

* See also Statutory Rules and Orders, 1926, No. 1621.

International Commission for Uniform Methods of Sugar Analysis*

REPORT OF THE PROCEEDINGS OF THE NINTH SESSION, 1936

THE Ninth Session of the Commission was held at the Institute of Chemistry, London, from August 31st to September 3rd, 1936, when eighty members attended, representing 20 nations. The President was Mr. Frederick Bates, U.S.A., and the Secretary was Mr. Lewis Eynon.

The constitution and by-laws of the Commission were discussed and adopted, and reports and recommendations on the following subjects were presented by the respective Referees, and adopted in each instance.

WEIGHING, TARING, SAMPLING AND CLASSIFICATION OF SUGARS.—It was recommended that uniform international methods of sampling should be elaborated, and that these methods should be based on the experience gained in Czechoslovakia, Germany, Great Britain, Java, Poland and the United States. The method of sampling must depend upon the conditions. The recommendation was made that the various sampling procedures now used in different countries should be made the subject of further study and report.

CONDUCTOMETRIC DETERMINATION OF THE ASH-CONTENT.—The conductometric method was prescribed in Czechoslovakia two years ago and has recently been introduced into Germany. In a study of a large number of determinations it was found that with raw beet sugars the agreement between the results obtained by the chemical and conductometric methods was very close (within 3 per cent. of the amount of ash), but with raw cane sugars the differences were much greater. Such differences are of importance only so long as the gravimetric method is prescribed as the standard method in the valuation of raw sugar. Apart from this, there is no reason for hesitating to introduce the electrometric method, which has the further advantage of giving only the percentage of soluble ash.

DETERMINATION OF REDUCING SUGARS AND THE INFLUENCE OF OVER-HEATING ON THE DETERMINATION OF INVERT SUGAR.—*Determination of Invert Sugar in Refined Sugars, Factory White Sugars, Raw Beet Sugars, Beet Molasses, and Cane Sugars of Low Invert Sugar-content.*—The type of method most likely to command general confidence as an international standard in place of Herzfeld's (which is not sufficiently accurate) is one in which Fehling's solution is replaced by a copper reagent of low alkalinity, containing sodium carbonate instead of hydroxide, and having only a very slight action on sucrose. The Referee (Mr. J. H. Lane) recommended that points of difference in Ofner's method (official in Czechoslovakia), the Luff–Schoorl method (official in Java), and a method worked out at the Berlin Sugar Institute, should be studied and their best features embodied in an International Standard Method for the Determination of Small Quantities of Invert Sugar in Sugar Products.

Determination of Invert Sugar in Raw Cane Sugars.—Recent studies have confirmed the accuracy of the Herzfeld method for cane sugars and indicated that the Munson and Walker method is less accurate. The Luff–Schoorl and Lane–Eynon methods are the most suitable for general use, the former avoiding large sucrose corrections, and the latter being rapid and simple in technique. The Referee recommended that the subject of defecation of cane sugars for invert sugar determinations should be studied.

Determination of Invert Sugar in Cane Molasses.—The Referee recommended

* Printed in England and published by the International Commission for Uniform Methods of Sugar Analysis. Chairman, Publication Committee: Lewis Eynon, 7 & 8, Idol Lane, London, E.C.3. 1937. Price 2s. Issued as a Supplement to *The International Sugar Journal*, January, 1937.

that comparative determinations should be made by the Munson and Walker, Lane–Eynon and Schoorl (Java) methods and by the Brown, Morris and Millar method, with particular regard to the concordance obtainable by different chemists with the same method.

The Report, with a slight amendment, was accepted. Detailed descriptions of some of the newer methods recommended for study are given.

DETERMINATION OF THE DECOLORISING POWER AND FILTERING QUALITY OF CHARS.—The Referee recommended that the quantities of carbons required to give the same decolorising effect as standard carbon (*e.g.* Carboraffin or Norit) should be studied, under standardised conditions (*e.g.* concentration, *p*H, temperature, duration of test, etc.). The relative rate of filtration of the carbon under test should be determined, and a method for determining the revivifying qualities of carbons be defined. The moisture, ash, and effect of the carbon on the *p*H of the solution should be determined; also the apparent sp.gr. and the rate of sedimentation by the method standardised by the Central Laboratory of the Polish Sugar Industry.

TESTING OF MOLASSES.—*Hydrochloric Acid Inversion.*—The Referee presented a critical survey of recent attempts to eliminate various sources of error in the determination of sucrose by acid inversion, and pointed out the desirability of neutralising the acid before the inverted solution is read and adding an equivalent quantity of sodium or potassium chloride to the defecated and de-leaded solution used for the direct reading. He pointed out further the possible effects of the salts present in molasses on the rotation of the sugars and non-sugars. The inversion constant used should be determined on sucrose in presence of the same quantity of salts as in actual analysis.

Invertase Inversion.—The Referee was unable to recommend invertase methods for commercial analysis, since they demand pure yeasts of a suitable culture.

The Report was adopted, together with a recommendation by Mr. C. F. Snyder that "In the analysis of cane and beet molasses the official methods of the National Bureau of Standards be adopted as tentative."

These methods, which are now official in the U.S. Customs Service and in the New York Sugar Trade Laboratory, are given in detail.

APPLICATION OF REFRACTOMETER METHODS TO SUGAR ANALYSIS.—The Referee gave a description of the new dipping refractometers of Zeiss and Askania with the Goldbach flow-through cell attachment, which enables a refractive index to be accurately determined to the fifth place of decimals.

The International Table of Refractive Indices of Sugar Solutions shown opposite was adopted. It is based on the figures of Schönrock–Landt (1933), Schönrock (1911) and Main.

International temperature correction tables for the normal model above and below 20° C. and the tropical model above and below 28° C. were also adopted.

THE 100° S POINT OF THE SACCHARIMETER.—It was suggested that the value 16·269 ± 0·002 g., weighed in air with brass weights, should be adopted as the official normal weight for the French saccharimeter scale. This would bring the International Sugar Scale and the French Sugar Scale into agreement.

STANDARDISATION OF QUARTZ CONTROL PLATES.—Recommendations as to (*a*) optical purity, (*b*) identification marks, and (*c*) plate mountings, were made. It was also suggested that the National Physical Laboratories in Washington, London, Berlin, and Paris should be requested to collaborate and determine: (i) the rotation, in circular degrees, of the 100° S plate for the wave-length (optical centre of gravity) obtained with the Osram sodium vapour arc lamp, (ii) the rotation in circular degrees produced by the Osram sodium vapour arc lamp for plates approximately 25, 50, 75 and 100 S.

EVALUATION OF REFINING QUALITIES OF RAW BEET AND CANE SUGAR.—For raw beet sugars the German type-system, based on colour after a standard affination

test, gives a useful measure of affinability, but fuller information as to the best conditions of affination can be obtained by the conductometric affination test. For raw cane sugars the methods of Harman and Honig were recommended.

INTERNATIONAL SCALE (1936) OF REFRACTIVE INDICES OF SUCROSE SOLUTIONS

Per cent.* Sucrose	n_D^{20}	Per cent.* Sucrose	n_D^{20}	Per cent.* Sucrose	n_D^{20}	Per cent.* Sucrose	n_D^{20}
0 ..	1·33299	22 ..	1·36719	44 ..	1·4076	65 ..	1·4532
1 ..	1·33443	23 ..	1·36888	45 ..	1·4096	66 ..	1·4555
2 ..	1·33588	24 ..	1·37059	46 ..	1·4117	67 ..	1·4579
3 ..	1·33733	25 ..	1·3723	47 ..	1·4137	68 ..	1·4603
4 ..	1·33880	26 ..	1·3740	48 ..	1·4158	69 ..	1·4627
5 ..	1·34027	27 ..	1·3758	49 ..	1·4179	70 ..	1·4651
6 ..	1·34176	28 ..	1·3775	50 ..	1·4200	71 ..	1·4676
7 ..	1·34326	29 ..	1·3793	51 ..	1·4221	72 ..	1·4700
8 ..	1·34477	30 ..	1·3811	52 ..	1·4242	73 ..	1·4725
9 ..	1·34629	31 ..	1·3829	53 ..	1·4264	74 ..	1·4749
10 ..	1·34783	32 ..	1·3847	54 ..	1·4285	75 ..	1·4774
11 ..	1·34937	33 ..	1·3865	55 ..	1·4307	76 ..	1·4799
12 ..	1·35093	34 ..	1·3883	56 ..	1·4329	77 ..	1·4825
13 ..	1·35250	35 ..	1·3902	57 ..	1·4351	78 ..	1·4850
14 ..	1·35408	36 ..	1·3920	58 ..	1·4373	79 ..	1·4876
15 ..	1·35567	37 ..	1·3939	59 ..	1·4396	80 ..	1·4901
16 ..	1·35728	38 ..	1·3958	60 ..	1·4418	81 ..	1·4927
17 ..	1·35890	39 ..	1·3978	61 ..	1·4441	82 ..	1·4954
18 ..	1·36053	40 ..	1·3997	62 ..	1·4464	83 ..	1·4980
19 ..	1·36218	41 ..	1·4016	63 ..	1·4486	84 ..	1·5007
20 ..	1·36384	42 ..	1·4036	64 ..	1·4509	85 ..	1·5033
21 ..	1·36551	43 ..	1·4056				

* Grams per 100 grams.

ELIMINATION OF ERRORS DUE TO LEAD CLARIFICATION IN POLARISING RAW SUGARS.—In view of the fact that the composition and physical properties of basic lead acetate preparations have an important influence on the results, the Referee recommended that the Commission should be authorised to devise suitable tests.

The relative merits of basic lead acetate in solution and in the dry state were discussed, and the following recommendation was adopted: "If no change in the sugar scale is or has been made, clarification shall be effected with standard lead subacetate solution (Third Session of International Commission, Paris, 1900); but if a change from the Herzfeld-Schrönrock scale to the International Sugar Scale is made, then clarification shall be effected with standard dry lead subacetate (Horne's Dry Lead, U.S. Trade Mark)."

DETERMINATION OF RAFFINOSE.—It was agreed that, in the present state of knowledge, the only methods that could be recommended on theoretical grounds were those depending on the use of enzymes. Any new method for the determination of raffinose must be judged by its capacity to give results in close agreement with those obtained with the basic methods, working with enzymes.

COLORIMETRY IN THE SUGAR INDUSTRY.—The Report recommended that spectrophotometry should be considered the basis of all colour measurements in the sugar industry, the measurements to be made with the monochromatic light of the mercury arc at 435·8, 546·1 and 578·9$m\mu$. It was recommended that an average absolute value suitable for the international definition of a Stammer degree should be published shortly. It is also intended eventually to standardise the preparation of sugar solutions for colorimetry.

CLERGET DIVISORS FOR THE MORE WIDELY USED INVERSION METHODS.—The three branches of the subject—*viz.* (i) Re-determination of Clerget divisor; (ii) specific effect of salts on the Clerget divisor; and (iii) re-determination of the temperature coefficient of the Clerget divisor—are to be submitted to further study.

DETERMINATION OF WATER IN SUGARS AND SUGAR PRODUCTS BY DRYING METHODS.—The following recommendations were accepted by the Commission:

(i) That the standard method for estimation of water in beet molasses, low ash cane syrup, golden syrups, should be carried out in vacuum ovens bled with dry air at 70° C., or preferably 60° C., with a pressure not exceeding 5 cm. Metal dishes with close fitting lids with knob should be used, and for 1 g. of solids approximately, 25 to 30 g. of 40–60 mesh white quartz sand, water being added to facilitate admixture with the sand and drying continued until 2 hourly weighings do not differ by 0·5 mg.

(ii) That refractometer solids corrected for invert sugar should be taken as equivalent to this, or made a subject for further study.

(iii) That the determination of water in cane molasses by drying in vacuum oven as in recommendation (i) should be studied further and compared with drying at lower temperatures, which may obviate decomposition loss being included as water.

Further, in order to obtain a more rapid method for cane molasses, a comparison between drying and refractometric methods, the latter corrected for invert sugar, should also be made to ascertain whether a correction based on ash or conductivity can be used to adjust the refractometer results to agree with those by drying.

DETERMINATION OF HYDROGEN ION CONCENTRATION OF SUGAR FACTORY PRODUCTS.—It was agreed to defer this subject until the next Session of the Commission.

ANALYSIS AND EVALUATION OF REFINED SUGARS.—The Referee suggested that, before the next Session of the Commission, a selection should be made of the tests most widely used in the valuation of refined sugar, that these tests should be investigated and recommendations drawn up for carrying them out in a uniform manner.

The next Session of the Commission was fixed for 1940, in Berlin.

U.S.A. Department of Commerce

National Bureau of Standards

INKS FOR RECORDING INSTRUMENTS*

INKS for recording instruments are made by dissolving dyes in a mixture of glycerin and water. They dry chiefly by being absorbed by the paper, and for this reason lines drawn with them have a tendency to "feather," or have irregular edges. The paper and the nature of the dye determine whether or not there will be feathering.

Instruments for making continuous records of temperature, barometric and steam pressures, electric voltage, etc., may have to run for a long time without attention, so that there must be an ample supply of ink of a kind that will not dry on the pen or freeze in winter. For many years the United States Weather Bureau has used recording ink made by dissolving a dye in a mixture of equal

* Research Paper R.P.935. By C. E. Waters. November, 1936.

volumes of glycerin and water, and for use in certain parts of the United States sufficient ethyl alcohol to keep the ink fluid at any winter temperature is added.

In experimental tests it was found that for indoor use a mixture of 1 volume of glycerin or glycol with 3 volumes of water is a much better solvent than a mixture of equal volumes of the two liquids, and that ethylene glycol is not as good as glycerin at either dilution.

To prevent feathering, as far as possible only the direct dyes should be used. The drawback to the use of some of these dyes is the comparative dullness of their hues. To remedy this, the concentrations were varied so as to get a sufficient depth of colour without causing feathering through non-absorption of some of the dye by the paper. Thus, Congo Red and Diamine Sky Blue FF showed feathering at a concentration of 10 g. per litre, but not at concentrations of 5 and 7·5 g. per litre, respectively. Of the black dyes, Erie Black RX00 could be used at concentrations of 12·5 and 15 g. per litre, and Erie Black RW at 11 g. and 12 g. per litre.

Three or four species of moulds were found on the corks and, in one instance, on the surface of inks prepared with glycerin and water after they had been kept for 3 months, but no mould could be detected on the corks that had been in contact with inks made with ethylene glycol.

Sir George Beilby Memorial Awards

THE Administrators of the Beilby Memorial Fund, consisting of the Presidents, Treasurers and Secretaries of the Institute of Chemistry, the Society of Chemical Industry and the Institute of Metals respectively, have announced awards of 100 guineas each to Dr. Bernard Scott Evans and Dr. William Harold Juggins Vernon.

Dr. Evans was educated at Faversham Grammar School and gained his first experience in chemistry in the laboratories of Mr. Leo Taylor, O.B.E., and subsequently with the late Mr. Lawrence Briant, with whom he continued working until the War. He also attended King's College, and graduated B.Sc. (Lond.) in 1904. He passed the Examination for the Associateship of the Institute of Chemistry in 1909, and was elected to the Fellowship in 1915.

In September, 1914, he enlisted in the Artists' Rifles, was gazetted to the Queen's Regiment in 1915, and proceeded to France to join the 4th Suffolks in 1916. In the following year he was seriously wounded and was awarded the M.C. Thereafter he was engaged on scientific work in the Chemical Warfare Department of the Ministry of Munitions, and received the decoration of M.B.E. Since 1919 he has been attached to the Research Department at Woolwich, where he now holds the position of a Scientific Officer. He was awarded the degree of Ph.D. (Lond.) in 1924 and D.Sc. in 1933. He has devised numerous analytical methods for the separation and determination of metals, and contributed the chapters dealing with the methods of analysis applicable to lead, bismuth, arsenic, antimony, tin, iron, chromium, and metallic constituents of steel in Mitchell's "Recent Advances in Analytical Chemistry."

Dr. Vernon received his scientific training at Aston Manor Technical School, Birmingham Municipal Technical School, the University of Sheffield and the University of Birmingham. He graduated B.Sc. (Birm.) in the first division in 1919, Ph.D. (Lond.) in 1924, and D.Sc. (Lond.) in 1927. During the War he served as a leading mechanic and petty officer (R.N.A.S.) at the Royal Naval Experimental Station, Stratford, and was subsequently engaged as Analyst in the Admiralty Laboratories in Birmingham, before resuming his academic post.

In February, 1921, he was appointed Investigator to the newly-formed Atmospheric Corrosion Committee of the British Non-ferrous Metals Research Association. This work, which in 1927 was taken over by the Department of Scientific and Industrial Research, included early quantitative determinations of invisible oxide films on metals, and established a number of generalisations on atmospheric corrosion phenomena (ferrous and non-ferrous).

Dr. Vernon was elected to the Associateship of the Institute of Chemistry in 1920, and to the Fellowship in 1927, in which year he received the Diploma of the Imperial College. His publications have included "A Bibliography of Metallic Corrosion" (Arnold), the First and Second Reports to the Atmospheric Corrosion Research Committee (each of which formed the subject of a General Discussion by the Faraday Society), and other papers in various Transactions or Journals.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Detection of Pectin in Milk Products. E. Letzig. (*Z. Unters. Lebensm.*, 1936, **72**, 312–319.)—The use of pectin in food products, especially in milk products, egg-confectionery, sweets, ice-cream and non-alcoholic drinks and also in soap, is likely to increase (Ziegelmayer, *Nahrungsmittelrundschau*, 1935, No. 9). Since it appears that its main use will be in milk products, the author has investigated the problem of its detection in milk, cream, curd and cheese. Pectin was added to these foods in the form of a commercial product, "Lattopekt," available in solid and liquid form. A preparation known as "acid Lattopekt" contains also an organic acid. Liquid Lattopekt contains about 5 per cent. of pectin. In dairy practice, chiefly in the manufacture of edible curds and cheese, the amount of the liquid preparation used varies from 0·25 to 0·5 per cent. of the food. The method for the determination of pectin depending upon its conversion into calcium pectate is not applicable to milk products, owing to the difficulty of obtaining a serum entirely free from albumin. Detection of pectin by liberation of methyl alcohol, for which delicate tests are available, has the disadvantage that large amounts of the sample are required. The method which the author has previously applied to the detection of other thickening agents (*Z. Unters. Lebensm.*, 1934, **68**, 301) has been successfully applied to the detection of pectin in milk products. For the experiments, amounts of Lattopekt varying from 0·25 to 8 per cent. were added to the foods. The serum prepared by acidification with acetic acid was freed from coagulable albumin by boiling and filtering, and its viscosity was determined in Ostwald's viscometer, the relative viscosity being expressed as the time of efflux of the serum, divided by the time of efflux of the same volume of water under the same conditions, the determinations being made at 20° C. The relative viscosity of pure milk serum is about 1·15 and varies only within narrow limits. On the addition of 0·25 per cent. of neutral Lattopekt the viscosity is raised to 1·18, and further additions give correspondingly higher values. The neutral and acid forms of the pectin preparation cause almost identical changes

in the viscosity. To determine whether pectin was adsorbed by the precipitated curd the same additions were made to the serum of untreated milk, and it was found that loss of pectin by adsorption is negligible. The following are examples of the figures obtained:

Neutral liquid Lattopekt, per cent.	0·25	0·5	0·75	1·0	2·0	4·0	6·0	8·0
Relative viscosity	1·19	1·23	1·27	1·32	1·49	1·92	2·60	3·29

Cream, after the addition of pectin, gives practically the same results as milk. Curd products are treated as follows:—By simple expression of about 100 g. of curd, 25 ml. of serum are obtained. This is acidified with a single drop of acetic acid, boiled and filtered, and the viscosity of the filtrate is determined. In experiments to determine the normal value for curd serum, it was found that the viscosity of the serum of freshly-prepared curd is approximately the same as that of milk, but that the viscosity increases as the curd ages, presumably because of changes which take place and increase the solubility of the albumin. During ten days' storage of a sample of curd the viscosity of the serum increased from 1·18 to 1·77. To remove this difficulty the viscosity of the curd serum was determined, after which the serum was subjected to the action of a pectin-splitting enzyme (pectolase) for one hour at 37° C., and, after the excess of enzyme preparation had been removed by filtration, the viscosity was again determined. The diminution in viscosity corresponds with the amount of pectin present. The enzyme was added in the form of a commercial preparation, "Bayer N" or "Filtragol." The enzyme had no effect upon the other constituents of the serum. The process was then applied to the examination of cheese. In order to avoid complications due to the presence of micro-organisms and moulds, the cheese to be examined was carefully freed from rind, and only the inner portion was used. Two large samples of cheese were prepared, one containing, and the other free from, pectin. These were stored under conditions favourable to normal ripening, and samples were taken from time to time. During the early stages of ripening sufficient serum could be obtained by simple expression, but in the later stages this became more difficult, and the serum was then obtained in the following manner:—The water-content of the cheese was determined and, after the cheese had been finely shredded, it was allowed to stand for a short time with an amount of water equal to its water-content. The serum was then pressed out, and the amount of added water was removed by evaporation. The viscosity of the serum was determined before and after action of the enzyme. Although, in every instance, the presence of pectin was indicated by a decrease in viscosity after treatment with enzyme, yet, in three weeks, the viscosity of the serum of the treated cheese, after enzymic action, was lower than that of the corresponding portion of the pectin-free cheese. Apparently a slight decomposition of pectin takes place during ripening. The viscosity of the serum of the freshly-prepared pectin-cheese was 1·13, and in three weeks the value had risen through intermediate values to 2·58. These values were unchanged by enzymic action. The cheese containing 0·5 per cent. of liquid Lattopekt gave serum of viscosity 1·21 when freshly prepared, and this value was reduced to 1·13 by enzymic action. The values in three days, one week, and three weeks (the corresponding reduced values after treatment with enzyme being given

in brackets) were respectively 1·74 (1·67), 1·74 (1·67), 2·43 (2·38). Provided that the enzyme preparation does not affect other substances which may be present, this method should prove of value for the detection of pectin in other food material.

A. O. J.

Discoloration and Corrosion in Canned Cream. C. J. Jackson, G. R. Howat and T. P. Hoar. (*Tech. Pub. International Tin Research and Dev. Council*, Series A, No. 49, 1937.)—Bronzing, purpling or blackening of tin cans containing cream has been found to be due to tin sulphides produced by the breakdown of proteins when the temperature or the duration of the sterilising process is excessive. The presence of a small amount of sodium bicarbonate, as commonly used as a stabiliser, is probably beneficial in preventing purpling of the can in storage. The existence of exposed steel on the internal surface of the can is detrimental and tends to give rise to black specks of ferrous sulphide in the cream; it is desirable, therefore, that the coating should be as free as possible from pores. S. G. C.

Effect of Time on the Iodimetric Method of Sugar Analysis. H. S. Miller. (*Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 37–38.)—When glucose and lactose were oxidised, under the same conditions, by an alkaline solution of iodine, the rate of oxidation was lower for lactose than for glucose. The reagents were as follows:—(A) Iodine in potassium iodide solution: 12·69 g. of iodine and 16·60 g. of potassium iodide were dissolved in distilled water and diluted to a litre. (B) Sodium thiosulphate solution: 24·8 g. of the salt were dissolved, and the solution was boiled, cooled and diluted to 2 litres. (C) Sodium hydroxide solution: $N/10$, free from sodium carbonate. (D) Starch solution: Prepared fresh daily. *Method.*—This was essentially that of Kline and Acree (*Ind. Eng. Chem., Anal. Edn.*, 1930, **2**, 413; Abst., ANALYST, 1931, **56**, 48). To 25 ml. of sugar solution in a flask with a ground-in stopper, the iodine and sodium hydroxide solutions are added alternatively in 4-ml. and 7-ml. portions respectively, with shaking after each addition. The temperature is kept at 25° C., and the time is measured from the addition of the iodine and alkali to the sugar solution to the stage at which the solution is acidified slightly with sulphuric acid. The excess of iodine is titrated immediately afterwards with (B). When 100 mg. of the sugar, 35 ml. of (C), and 20 ml. of (A) were used, the optimum time for the oxidation of glucose was 8 minutes; beyond this, over-oxidation occurred. With 100 mg. of lactose monohydrate, only 92 per cent. was oxidised in 8 minutes, but when the amount of iodine solution was increased to 25 ml., optimum oxidation occurred in 15 minutes. A mixture of equal weights of these sugars (50 mg. of each) was more difficult to oxidise than 100 mg. of either, but when 100 mg. of sucrose were added to this mixture, oxidation was complete in 5 minutes and over-oxidation occurred in 15 minutes. The sugars used were glucose, $[\alpha]_D^{25°}$ 52·45 and lactose monohydrate, $[\alpha]_D^{25°}$ 52·90. Optical measurements showed 99·68 per cent. to be the sucrose-content of the sample used. E. B. D.

Development of Acidity in Palm Oil. R. Wilbaux. (*Bull. Matières gras.*, 1936, **20**, 255–257.)—The existence of a lipase in the pericarp of the fruit of *Elaeis guineensis* is confirmed, and its action may be considerably augmented by the presence of mould fungi, particularly of *Mucor* sp., which develop on the site of

wounds and at the point of insertion of the drupe stalk. *Aspergillus glaucus* and an oospore type of *Hyphomycetes* have also been found. The lipase action is closely related to the cytoplasmic content and to the presence of calcium ions. Hydrogen ions are deterrent. The action of the lipase diminishes with the increase of free fatty acids, ceasing theoretically when the titre is 45 per cent. The development of rancidity in the fresh oil is not due to the presence of an oxidase in the pulp, nor to enzymes secreted by moulds, etc. Carotene may act as an oxidising catalyst, but the increase in aldehyde in the oil during commercial extraction is small. Storage of the fresh oil in glass vessels causes an increase in acidity of about 0·5 per cent. in 55 days, but this is less if brown glass is used, and less still in iron tanks. Centrifugal treatment of the oil makes it a less favourable medium for mould growth. The fruit should be brought to a temperature of 55° C. as quickly as possible so as to kill the lipase rapidly, and sterilisation of the whole charge will give the best oil, but as this involves conveyance of an extra 50 to 60 per cent. of inert material to the factory the cost of transport and of manual labour may render it impossible. Where manual cleaning is used, certain precautions may be taken to prevent infection by moulds, etc., such as spreading instead of heaping the fruits, cementing of walls and floors, and periodical cleaning with antiseptic solution. D. G. H.

Rancidity in Fats. I. The Effect of Low Temperatures, Sodium Chloride, and Fish Muscle on the Oxidation of Herring Oil. A. Banks. (*J. Soc. Chem. Ind.*, 1937, **56**, 13–15T.)—The catalytic effect of salt on the development of rancidity in bacon fat during storage (Lea, ANALYST, 1931, **56**, 759) is difficult to explain from known data, and the present investigation seeks to elucidate it. The herring oil used was extracted with petroleum spirit from summer herring caught off Fraserburgh, and the course of oxidation was followed by determining the peroxide-content of the fat by a modification of Lea's method. At −5° C. the formation of peroxides reached a maximum in about 45 days, at −10° C. in 110 days, and at lower temperatures it was doubtful if the maximum was reached in 200 days. To find the effect of sodium chloride on oxidation, a volume of lime water requiring 0·55 g. of palmitic acid to neutralise it was made up to 50 ml. with water containing 2·5 g. of salt, and shaken with 50 g. of herring oil containing 0·6 g. of palmitic acid, in an Erlenmeyer flask in which the air had been replaced by nitrogen. Exactly 10 g. of the emulsion were then placed in each of a series of Petri dishes and left at −5° C., together with controls without salt. At intervals dishes were removed, and, after the emulsion had been desiccated with anhydrous sodium sulphate (alkali-free), the oil was extracted with petroleum spirit and the solvent was distilled off, the last traces being removed in a stream of nitrogen under slightly reduced pressure. It was found that sodium chloride had no effect on the rate of atmospheric oxidation of herring oil. Herring muscle (30 g.), water (20 g.), and herring oil (50 g.) were mixed and then emulsified, in some instances with addition of 0·3 g. of sodium chloride, and it was found that the progress of oxidation was of the normal type, but more pronounced in the presence of herring tissue, and still more pronounced when salt was present. The catalytic effect of the muscle was destroyed by heat. It is suggested that an oxidative enzyme system is present in herring muscle. D. G. H.

Studies on the Nature of Antioxygens Present in Natural Fats. III. Occurrence of Antioxygenic Compounds in Extracted Soya-bean Oil cake. T. G. Green and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1937, **56**, 23–26T; *cf.* ANALYST, 1932, **57**, 320, etc.)—The residual material of seeds after extraction of the fatty oil contains considerably higher proportions of oxidation-retarding compounds than the oil itself, but the material requires special treatment before these compounds can be extracted. The preparation of an active anti-oxygenic concentrate from soya-bean cake is described. The extracted meal, after digestion with dilute solutions of organic acids, such as 2 per cent. acetic acid in water or acetone, yields about 10 per cent. of material when heated with methyl alcohol. The part of this extract soluble in cold acetone (about 2 per cent. of the meal) is a viscous gum which, in 0·2 per cent. concentration in distilled unsaturated fatty esters, exerts a marked retarding action on the oxidation of the esters by air at 97·5° C. This concentrate is similar in physical and chemical properties to Olcott and Mattill's material obtained from the unsaponifiable fractions of wheat-germ, cotton-seed or palm oils (*J. Amer. Chem. Soc.*, 1936, **58**, 1627), and also to Dean's concentrate from linseed "foots." The yield of concentrate from the extracted cake is many times greater than from the fatty oils, and the anti-oxygenic compound removed from the seeds with the oil seems to be 2 or 3 per cent. of the total present in the cake, which, however, cannot be removed without a gentle acid treatment followed by an alcoholic solvent. Cellulose has been found not to be the original source of the anti-oxygenic compounds, and organic phosphorus compounds are not regarded as a likely source. D. G. H.

Optical Rotation and Refractivity of Nicotine and Nicotine Sulphate in Dilute Aqueous Solution. F. G. H. Tate and L. A. Warren. (*J. Soc. Chem. Ind.*, 1937, **56**, 39–40T.)—The pure nicotine used for the determinations was prepared from the crude material by Lowry's modification of Ratz' method (*J. Chem. Soc.*, 1929, 1376), and had the following constants:—d_4^{20}, 1·0096; $[\alpha]_D^{20}$, −169·4°; $[\alpha]_{546\cdot1}^{20}$, −204·2°. The specific rotation, the rotation of mean yellow light measured in sugar (Ventzke) degrees, and the refraction by the Zeiss immersion refractometer were determined for aqueous solutions of nicotine and nicotine sulphate at concentrations of 0 to 10 per cent. The values of the specific rotations were constant for each substance: for nicotine $[\alpha]_D^{20}$, −79·4°; $[\alpha]_{546\cdot1}^{20}$, −96·1°; and for nicotine sulphate $[\alpha]_D^{20}$, +14·3°; $[\alpha]_{546\cdot1}^{20}$, +17·2°. The Zeiss readings for both nicotine and nicotine sulphate solutions increased proportionately with the concentrations from 0 to 10 per cent.: 5·41 units per 1 per cent. increase in concentration for nicotine, and 5·13 units for nicotine sulphate. D. G. H.

Alkaloids of the Genus *Senecio*. J. J. Blackie. (*Pharm. J.*, 1937, **138**, 102–104.)—This genus of plants, which is used medicinally, contains appreciable amounts of well-defined alkaloids. British species are considered harmless, but those of Canada, New Zealand, South Africa, and Norway have caused diseases in cattle, and in South Africa cases of illness and death have been traced to flour ground from wheat containing seeds of *Senecio ilicifolius* and *S. burchelli*. The symptoms were gastric disturbance with enlargement of the liver. There are two groups of *Senecio* alkaloids: I. Alkaloids very soluble in chloroform and

containing 18 carbon atoms. II. Alkaloids partly soluble in water, very soluble in chloroform, and containing 12 carbon atoms. In this investigation three South African and twelve British species have been examined. The South African species contained alkaloids of Group I. Alkaloids of this group were also found in nine of the British species, and those of Group II in three British species. The alkaloid-content of the South African species was much higher than that of the British ones. *S. isatideus* (poisonous ragwort or Dan's cabbage), which is widespread in South Africa, contained 1·14 per cent. of isatidine, a new alkaloid, and 0·15 per cent. of retrorsine. Retrorsine was also present in the other South African species. *S. glaberrimus* contained 0·027 per cent., and *S. venosus* 0·01 per cent., of retrorsine. The results for British species were as follows:

Species	Alkaloids Per Cent.	Date
Senecio vulgaris (groundsel) ..	0·015	April
	0·06	June
	0·015	September
S. squalidus	0·06	July, 1935
S. viscosus	0·06	July, 1934
	0·28	Early summer
S. Jacobaea (common ragwort)	0·03	June, 1934
	0·057	July, 1934
S. aquaticus (marsh ragwort) ..	0·04	July
	0·018	September
S. cineraria	0·052	
S. erucifolius	Trace	
*S. paludosus**	0·0015	
*S. palustris**	0·001	

* These species, being rare in this country, were obtained from Holland.

The alkaloid of the April and September groundsel was pure senecionine; this was also present, together with another alkaloid, in the June sample. It occurred pure in *S. viscosus* and, mixed with a little squalidine (a new alkaloid), in *S. squalidus*. Alkaloids of the other species were difficult to obtain pure and are still being investigated. Group II.—Alkaloids of this group were present in *S. sylvaticus*, *S. saracenicus*, and *S. campestris*, var. *maritimus*. They were obtained as syrups, and were usually purified by fractional crystallisation in a high vacuum.

Method of analysis.—The coarsely powdered dried substance was extracted repeatedly with alcohol until the alcoholic extract gave no reaction with Mayer's reagent. The alcohol was distilled off *in vacuo*, and the extract, which contained much chlorophyll and resinous matter, was then treated with 2 per cent. hydrochloric acid and filtered, and the colouring matter was removed from the filtrate by extraction with ether. The filtrate was made alkaline with ammonia, and the alkaloids were extracted by shaking with successive quantities of chloroform. By repeating the treatment with acid and chloroform the alkaloids were obtained in crystalline condition. Group II.—The general process of extraction was as described above, but, as the alkaloids were obtained as syrups, further treatment was necessary. Details of the methods of separation, purification and identification of the individual alkaloids in the various species examined are given for both

groups, and the constitutions of those of Group I are discussed. All alkaloids of this group yield the basic fission product retronecine, $C_8H_{15}O_2N$, which on reduction yields retronecane, $C_8H_{15}N$, which is isomeric with the tropane of solanaceous alkaloids and with heliotrin, an alkaloid of *Heliotropium lassocarpum*. All the *Senecio* alkaloids appear to have a heterocyclic five-membered ring which gives the pyrrole reaction by distillation with zinc dust. Senecionine and squalidine were described by Barger and Blackie (*J. Chem. Soc.*, 1936, 743). E. B. D.

Determination of Lipase in Official Preparations of Pancreatin. H. Penau and J. Guilbert. (*J. Pharm. Chim.*, 1937, **25**, 5–17.)—The method recommended is as follows:—A 1 per cent. solution of agar-agar is made up by swelling 10 g. of agar-agar, cut into small pieces, in about 200 ml. of water for 4 hours, straining through gauze, and dissolving the agar-agar in 800 ml. of boiling water, with constant stirring. The *p*H is adjusted to 7 by adding a few drops of dilute sodium hydroxide solution, the weight is made up to 1000 g., and the liquid is heated in an autoclave at 120° C. for 15 minutes, and filtered through a hot funnel. Twenty-ml. portions are sterilised in test-tubes, closed with sterilised cotton, for 20 minutes at 115° C., and covered with sterilised rubber caps to prevent evaporation. Into a 60-ml. flask with ground glass stopper are put, in the order given, 0·6 g. of glycine, 2 ml. of *N* sodium hydroxide solution, and 8 ml. of distilled water warmed to 40° C., followed by 40 mg. of a mixture of pancreatin and lactose (1 per cent. of pancreatin). The mixture is carefully shaken and treated with 10 ml. of the 1 per cent. agar-agar solution (warmed to 40° C.), and 1·5 ml. of purified tributyrin. After shaking, the liquid is kept in a water-bath at 40° C. for 2 hours; during the first half-hour the flask is shaken for 30 seconds every 5 minutes, and then for 30 seconds every 10 minutes. The *p*H must still be greater than 8·4 (pink with phenolphthalein). The action of the enzyme is stopped by the addition of 1 ml. of a 10 per cent. solution of sodium metaphosphate and 5 ml. of *N* sulphuric acid. The flask is shaken and cooled in a refrigerator. Extraction with ether is carried out at once or within 3 hours after this. The contents of the flask are transferred to a 300-ml. separating funnel, and the flask is washed out twice with 3 ml. of distilled water, first the stopper and then the neck being washed each time. The aqueous solution is extracted four times with ether, 50 ml. being used for the first and 25 ml. for the later extractions. The ethereal extracts are combined and washed, first with 2 ml. and then with 1 ml. of distilled water, and transferred to a 500-ml. conical flask. Fifty ml. of absolute alcohol and 10 ml. of water are added, and the liquid is titrated with *N*/10 sodium hydroxide solution to the end-point of bromophenol blue (1 ml. of a 0·04 per cent. solution). A blank test is made on an aqueous solution previously boiled for 2 minutes. It is suggested that for a pancreatin of Codex quality the difference between the two titration values should not be less than 10 ml. of *N*/10 sodium hydroxide solution. E. M. P.

Distinguishing Reactions of the Principal Silver Colloids. R. Deschaseaux. (*J. Pharm. Chim.*, 1937, **25**, 29–30.)—Vaille (*J. Pharm. Chim.*, 1934, **19**, 256; Abst., ANALYST, 1934, **59**, 422) has proposed reactions for distinguishing between argyrol, collargol, electrargol, and protargol. In the present

paper, tests are described for discriminating between 1 per cent. pseudo-solutions of collargol, argyrol, vitargyl, silver vitellinate, and silver proteinate. One ml. of the pseudo-solution is treated with 1 ml. of a solution containing crystallised sodium thiosulphate 10 g., dry sodium chloride 1 g., and distilled water to 100 ml. Collargol, argyrol, and vitargyl give precipitates with this reagent. After 30 minutes the flocculate is filtered off. For the second test the biuret reaction is applied to the filtrate from the first. The liquid containing collargol is the only one that does not give the reaction. For distinguishing argyrol from vitargyl, and vitellinate from proteinate, 2 drops of pure crystallisable acetic acid are added to 1 ml. of the pseudo-solution. Vitargyl and vitellinate give immediate precipitates with the acid. E. M. P.

Biochemical

Determination of the Place of Absorption of Halogen Derivatives of Ethylene in the Body. Le Bihan. (*J. Pharm. Chim.*, 1937, **25**, 20–23.)—Dogs were given repeated inhalations of the vapour of the solvent under examination, and were finally killed after a large dose. The organs were reduced to pulp and heated in a water-bath in the presence of a dilute solution of tartaric acid, while a current of air is drawn through them by means of the following train of apparatus:—A bubbler containing silver nitrate solution, the flask containing the organ, a second silver nitrate bubbler, all immersed in the water-bath, a quartz tube heated to 1000° C. in an electric furnace, a third silver nitrate bubbler, and a final bubbler to detect any residual hydrogen halide. The silver halide precipitated in the third bubbler was determined, and the quantity of solvent given up by the organ was calculated. The results of one experiment were as follows:

Animal: dog weighing 11 kg., given 7 doses of anaesthetic, the duration of the last dose being 50 minutes.

Organ	Weight of organ taken g.	Tetrachloroethane estimated mg.	Mg. of tetrachloroethane per 100 g. of organ
Bone marrow ..	0·60	0·518	85·92
Suprarenals	1·158	0·814	70·34
Thyroids	0·818	0·408	49·92
Brain	24·8	3·957	15·91
	35·2	6·856	19·4
Kidney	23·62	3·102	13·13
	22·60	2·929	12·97
Blood	30 ml.	3·2	10·66
	24 ml.	2·65	11·04
Liver	56·35	40·15	71·2
	51·6	43·3	83·8
Lungs	20·70	12·85	62 08
Testes	17·42	1·27	7·28
Pancreas	10·26	1·27	12·37
Abdominal fat ..	11·89	10·83	91
Spleen	13·25	0·804	6·07
Muscles	47·23	2·604	5·51
Urine	30 ml.	2·55	8·5

The anaesthetic was absorbed in large quantities by the organs rich in lipoids, the liver, brain, spleen, and lungs, and also by the endocrine organs, the suprarenals, thyroids, and particularly the marrow of the bones. In a further experiment to determine how long the anaesthetic was retained, samples of blood from anaesthetised dogs were removed periodically and examined. The results were as follows:

Dog anaesthetised for 10 *minutes.*

Time	Tetrachloroethane per 100 ml. of blood mg.
During anaesthesia	10
1 hour 50 minutes later	7·33
3 hours 30 minutes later	7·08

Dog anaesthetised for 13 *minutes.*

Time	Tetrachloroethane per 100 ml. of blood mg.
During anaesthesia	12·7
3 hours 45 minutes later	9·95
8 hours later	4·91
27 hours 15 minutes later	0·864

E. M. P.

Determination of Bases from Animal Tissues. E. Strack and H. Schwaneberg. (*Hoppe Seyler's Z. phys. Chem.*, 1936, **245**, 11–18.)—It has been found possible to use ammonium reineckate for the separation of choline from carnitine or betaine and to determine the amount of each present in solution. The chlorides of choline and carnitine are dissolved in about 500 times their weight of water at room temperature, made definitely alkaline to litmus with ammonium hydroxide, and an excess of ammonium reineckate solution is added. The solution must not be more concentrated or carnitine reineckate will be carried down by the choline salt and require a considerable amount of washing for its separation. After standing for about 30 minutes, fine silky crystals of choline reineckate are precipitated. These are filtered off, washed with a little water, dried and weighed. If the filtration is difficult, a little kieselguhr may be added; the choline reineckate is then removed by washing with a mixture of acetone and water, the solution is evaporated, and the residue is weighed. The choline reineckate is decomposed by the addition of silver sulphate and barium chloride, and the choline is assayed biologically as the acetyl derivative. Larger amounts may be identified chemically as the gold salt (long standing in ammoniacal solution and subsequent drying causes decomposition of part of the reineckate so that the acetone-water mixture will not dissolve it completely and the biological assay is low). For the determination of carnitine or betaine the ammoniacal filtrate from the choline precipitation is made acid to Congo red with hydrochloric acid, and more ammonium reineckate is added. The solution is allowed to stand for one hour on ice, after which the crystals are filtered off, with the aid of suction, washed with a little cold acidified water, dried and weighed. After decomposition, a portion may be acetylated and assayed biologically and the rest converted into

the gold salt. By this method it is claimed that small amounts of choline in the presence of betaine or carnitine can be separated with a fair degree of accuracy. Betaine reineckate behaves in the same way as the carnitine salt. S. G. S.

Studies on Ketosis. Quantitative Studies on the Oxidation of the Ethyl Esters of the Fatty Acids. H. J. Deuel, L. F. Hallman, J. S. Butts and S. Murray. (*J. Biol. Chem.*, 1936, **116**, 621–639.)—The administration of ethyl acetoacetate, ethyl butyrate or ethyl caproate to fasting rats resulted in a uniform ketonuria which was somewhat lower than that produced by the sodium salts of the acids. More than twice the degree of ketonuria was observed after the ingestion of the ethyl esters of caprylic, capric, lauric and myristic acids than was found in the acetoacetate controls. This was held to indicate that two fragments capable of forming acetone bodies are produced per molecule of fatty acids. When ethyl palmitate or ethyl stearate was administered in oil in one-eighth the dose employed in the above tests, or ethyl oleate without oil in a somewhat larger dose, the excretion of acetone bodies was greater than that with the laurate or caprylate controls. This suggests that the molecule of palmitic, stearic or oleic acid breaks up into at least three fragments, which are capable of being converted into acetone bodies. No appreciable ketonuria followed the administration of the ethyl esters of propionic, valeric, heptoic, pelargonic or undecylic acid. It is suggested that caproic and butyric acids, as well as the odd-chain carbon acids, break down chiefly by β-oxidation. The even-chain carbon acids containing 8 to 14 carbon atoms are probably also broken down by δ- and ζ-oxidation by "multiple alternate oxidation," as suggested by Jowett and Quastel. Since ethyl caprate is as good a ketogenic agent as ethyl caprylate, it is possible that its chief mode of oxidation is to acetone bodies rather than to dicarboxylic acids as suggested by Verkade and van der Lee. Acetone is the only important β-ketone excreted in the urine after the administration of the higher even-chain fatty acids. S. G. S.

Fluoresceinuria. G. Discombe. (*Lancet*, 1937, **232**, 86.)—If a urine is normal in colour but has an intense grass-green fluorescence, the presence of fluorescein should be suspected. If it is present, an absorption band between 506 and 482$m\mu$ (maximum at 494$m\mu$), *i.e.* almost identical with that of urobilin, with general absorption on the blue side of 430$m\mu$, can be observed. Both the fluorescence and absorption band disappear if the urine is acidified with hydrochloric acid. Ephazone, a proprietary remedy for asthma, produces these effects, most of the dye being excreted during the 4 hours after administration, although excretion is still incomplete after 8 hours. The dye is separated by acidifying 50 to 500 ml. of urine with 1 to 2 ml. of conc. hydrochloric acid and extracting with 25 ml. of amyl alcohol. The extract is then itself extracted, first with 100 ml. of water containing 20 drops of a 40 per cent. sodium hydroxide solution, and then with 50 ml. of water, 50 ml. of (presumably ethyl) alcohol being added to the combined washings, which are then diluted to 250 ml. The solution should be clear, and if 1 part of dye was present in 5,000,000 parts of the urine it should show the characteristic fluorescence, absorption and yellow colour. The dye may be identified by converting it into eosin (*cf.* Grant, ANALYST, 1936, **61**, 400), 100 ml.

of the solution acidified with hydrochloric acid being mixed with 1 ml. of bromine water and made alkaline with sodium hydroxide, when the liquid becomes pink and has a yellow-green fluorescence. Fairly concentrated solutions have an absorption band between 515 and 525$m\mu$ (b to E lines), but thick layers of liquid should be examined if the solution is dilute, as an excess of bromine may have destroyed some of the eosin. The fluorescence test provides a more sensitive test for both dyes than the absorption band. Solutions of eosin in water (or dilute ethyl alcohol) and in amyl alcohol showed, respectively, one band between 434 and 560$m\mu$ (maximum at 515 to 525$m\mu$), and one or two bands, according to the concentration, at 532$m\mu$ (intense) and 496$m\mu$ (weak and diffuse). Eosin in urine may be identified by extracting a mixture of 200 ml. of sample and 1 to 2 ml. of strong hydrochloric acid with 25 ml. of amyl alcohol, and examining the extract after addition of an excess of solid sodium acetate. A 1-inch layer of extract from urine containing 1 part of eosin in 5,000,000 showed the band at 532$m\mu$. One hour after the administration of 0·1 g. by the mouth the dye was present in the urine, but it could not be detected after the sixth hour. J. G.

Irradiation of Fats. Some Observations on Methods of Analysis of Oxidised Fats and on the Interrelation of the Results obtained. L. H. Lampitt and N. D. Sylvester. (*Biochem. J.*, 1936, **30**, 2237–2249.)—A method of evaluating the intensity of the Kreis test colour by the use of the Zeiss photometer; an improved method of determining the Issoglio value, incorporating the use of a stream of nitrogen for stirring the fat during the period of aqueous extraction; and a modification of Lea's method for the determination of peroxides are described. For full details of these methods the original paper should be consulted. The peroxide value after the Issoglio determination showed a decrease of 16 per cent. on that obtained before this determination, the Kreis test intensity was reduced by about 55 per cent., and the aldehyde value by about 55 per cent. from the same cause. These figures were independent of the degree of oxidation of the fat. The Issoglio value appeared to be proportional to the reduction in the aldehyde value and also to the aldehyde value of the original fat. The peroxide and aldehyde values were roughly proportional, and therefore the former was also proportional to the Issoglio value. S. G. S.

Isolation of the Antirachitic Vitamin from Halibut-liver Oil. H. Brockmann. (*Hoppe-Seyler's Z. phys. Chem.*, 1936, **245**, 96–102.)—From 150 kg. of halibut livers 300 g. of a concentrate containing 120 international units of vitamin D per mg., and 2000 C.L.O. units of vitamin A per mg. were prepared by the method described in the German patent, D.R.P. 634,760. When 130 g. of this concentrate were dissolved in benzine and the solution extracted 16 times with 90 per cent. methanol, the benzine solution yielded 58·5 g. of fraction (i) containing 700 C.L.O. units of vitamin A per mg., and the methanol extract contained 49·5 g. of fraction (ii) containing 2500 C.L.O. units of vitamin A per mg. Fraction (i) was then dissolved in benzine, and the solution was extracted 12 times with 95 per cent. methanol. From the benzine solution 23 g. of fraction (iii), containing 400 C.L.O. units of vitamin A per mg., was obtained, and the methanol extract contained 24 g. of fraction (iv) whose vitamin A content was 1000 C.L.O. units

per mg. Fraction (iv) was dissolved in benzine and extracted with 90 per cent. methanol. From the benzine solution 20 g. of fraction (iv*a*) was obtained. This had a vitamin *A* content of 470 C.L.O. units per mg. and a vitamin *D* content of 600 international units per mg. Fraction (iv*a*) was then subjected to adsorption on aluminium hydroxide III. For this purpose 27 g. were mixed with 200 mg. of Indicator-red 33 and dissolved in a mixture of one part of benzine and four parts of benzene. The same solvent was used for washing the column. Elution of the aluminium hydroxide gave 8·5 g. of an oily substance [fraction (v)], and from the filtrate 16·7 g. of fraction (vi) (also an oil) were obtained. When this process was repeated with 7·5 g. of fraction (vi), four zones were obtained. Zone 2, which consisted of the red colour and the vitamin, contained 2·9 g. of fraction (vii), which had a potency of 2400 international units of vitamin *D* per mg. The other zones were neglected. The process was repeated, using 6 g. of fraction (vii) and the same solvent as before. Three zones were obtained, Zone 1 was neglected, Zone 2 contained 2·85 g. of an oil having a vitamin *D* content of 5000 international units per mg. and Zone 3 contained 0·3 g. of an oil with an activity of 6000 international units per mg. Zone 2 became a fraction (viii) and Zone 3 fraction (ix). From fraction (viii) the sterols were removed, first by freezing and finally by precipitation with digitonin. The difference between these fractions was due to different sterol contents. Both fractions were then esterified with 3:5-dinitrobenzoylchloride in pyridine. The ester from fraction (viii) was again subjected to the chromatogram, the zone containing the vitamin was extracted with acetone, and after the addition of methanol the ester was allowed to crystallise. The crystals were extracted with petroleum spirit, in which the vitamin ester was soluble and the residue was found to consist of the esters of the higher alcohols. When the residue from the petroleum spirit solution was recrystallised, a product melting at 126° C. was obtained. After further recrystallisation from diluted acetone the m.p. had risen to 128°–129° C., and showed no depression when mixed with the 3:5-dinitrobenzoate from tunny-liver oil or with that from irradiated 7-dehydrocholesterol. The carbon and hydrogen percentages obtained by analysis agreed with those for the theoretical formula. When fraction (ix) was subjected to the same procedure, similar results were obtained. It is therefore claimed that the antirachitic vitamin isolated from halibut-liver oil is the same as that previously obtained from tunny-liver oil, and that both are identical with vitamin D_3.

S. G. S.

ABSTRACTOR'S NOTE.—In each instance the ester has been isolated and identified. The crystalline vitamin has not yet been obtained.

Influence of Fertilisers on the Carotene and Vitamin *C* Contents of Plants. J. B. H. Ijdo. (*Biochem. J.*, 1936, **30**, 2307–2312.)—When spinach was used as the experimental plant it was found that an increase in the nitrogen-content of the soil resulted in an increase in the carotene and vitamin *C* contents of the leaves. When the amount of potassium in the soil was increased, the carotene-content decreased, but the vitamin *C* content was increased. Under the conditions of the experiments the influence of calcium salts, magnesium salts or phosphates was negligible. It is suggested that there is a relationship between vitamin *C*

content and photosynthesis on the one hand, and between the chlorophyll-content and carotene on the other hand. It was found that analyses had to be made rapidly, for storage for a few days, even in ice, caused a large reduction in the amount of vitamin *C* found. S. G. S.

Amount of Ascorbic Acid in Blood and Urine. The Daily Human Requirements for Ascorbic Acid. M. van Eekelen. (*Biochem. J.*, 1936, **30**, 2291–2298.)—The ascorbic acid content of the blood, and the amount excreted in the urine, depend upon the quantity ingested and the amount stored by the organism. Saturation of the organism coincides with a certain level in the blood (about 13 mg. per litre). When this level is passed, the surplus amount is excreted in the urine. The determination of the ascorbic acid content of the blood has proved to be the most reliable means of ascertaining the state of saturation of the organism. The daily requirements are dependent on the amount stored by the organism and are largest when the subject does not become markedly unsaturated. The daily dose for adults weighing 70 kg. is about 60 mg. under normal conditions. In all the determinations carried out, interfering substances were removed by precipitation with mercuric acetate in accordance with previously described technique. (See also the following abstract.) S. G. S.

Relation between Diet and Urinary Output of Thiosulphate (and Ascorbic Acid). Human Requirements for Vitamin *C*. M. Heinemann. (*Biochem. J.*, 1936, **30**, 2299–2305.) The urinary output of ascorbic acid, determined after treatment with mercuric acetate, has been found to be independent of the amount of protein in the diet. The total reducing capacity of the urine, however, rises and falls in direct relationship to the quantity of protein in the food and depends chiefly on the output of thiosulphate. The amino-acids containing sulphur are probably the source of the thiosulphate in the urine, for, when cystine is ingested with a low protein diet, the effect on the total reducing capacity of the urine is the same as when the diet contains a large amount of protein. The daily requirement for man was found to be 60 mg. for a body weight of 70 kg. (See previous extract.) The same amount was required when 25 or even 37·5 mg. of "Redoxon" per day had been taken. This is regarded as *the actual requirement*, and from this work and other published results the *indispensable minimum* appears to be about half this amount. S. G. S.

Estimation of Ascorbic Acid as Furfural and a Comparison of Results obtained by this Method and by Indophenol Titration. J. H. Roe. (*J. Biol. Chem.*, 1936, **116**, 609–619.)—The method consists essentially in the estimation of the furfural formed by boiling an acid extract of a tissue, in which the ascorbic acid has been oxidised by shaking in presence of Norit, with hydrochloric acid alone and with hydrochloric acid containing stannous chloride. The difference between these values is the amount of furfural from ascorbic acid. Furfural is determined by the colour formed with aniline, stabilised with stannous chloride and proper amounts of acetic acid. The hydrochloric acid solution of stannous chloride is prepared by adding 5 parts of conc. hydrochloric acid to 1 part of water and dissolving 4 g. of stannous chloride in 40 ml. of this solution. The Norit is prepared

by placing 100 g. of Norit in a large flask, adding 1 litre of 10 per cent. hydrochloric acid and heating to boiling, filtering the suspension with the aid of suction, and washing with water until the washings are free from chlorides. The carbon is then heated gently until the water has evaporated and finally to redness for 15 minutes. An alcoholic solution of aniline is prepared by dissolving 1 part of colourless re-distilled aniline in 2 parts of 95 per cent. ethyl alcohol. If ascorbic acid is used as the standard solution, the standards must be freshly prepared each day. It has been found possible to use as a standard a solution of xylose in a saturated aqueous solution of benzoic acid, of such strength that 1 ml. is equivalent to 0·1 mg. of ascorbic acid. This solution must be compared with one of ascorbic acid for furfural formation, but the authors found that, under their conditions, 123 mg. of xylose in 1 litre of saturated benzoic acid solution gave the required values. The ascorbic acid in plant tissues is estimated by grinding 10 g. of the tissue in a mortar with sand under about 50 ml. of a 1 per cent. solution of oxalic acid. A funnel containing a mat of gauze is placed in a 100-ml. volumetric flask and the ground material is poured upon the gauze. The gauze is sqeezed until fairly free of solution and the solid material is returned to the mortar. About 10 ml. of the oxalic acid solution are added, and the mixture is ground again and returned to the gauze filter. The material on the filter is squeezed dry and washed with the oxalic acid solution which has been used previously for washing the sand in the mortar. The washing is continued until the fluid in the flask reaches the 100-ml. mark. The contents of the flask are mixed thoroughly, and 20 ml. of this solution are now placed in a small flask and solid calcium carbonate is added in excess. When the solution has been neutralised (as indicated by Congo red paper), 1 g. of Fleischmann's yeast is added. A pure strain of yeast, free from vitamin "supplements" should be used, or difficulty will be experienced in clarifying with charcoal. The flask is stoppered loosely and placed in an incubating oven at 38° C. until the fermentable sugar has been removed (about 1 hour). The liquid is transferred to a centrifuge tube, and the solids are removed by centrifugation. Ten ml. of the clear liquid are added to 2 ml. of glacial acetic acid in a small flask. About 0·5 g. of the acid-washed Norit are added, and the flask is shaken for 2 minutes, after which the solution is filtered.

For the estimation of total furfural, 1 ml. of the filtrate from the Norit treatment is placed in a test-tube, about 15 × 200 mm. In each of three similar tubes is placed 1 ml. of standard ascorbic acid (xylose) solution, such that the standards are equivalent to 0·1, 0·05 and 0·03 mg. of ascorbic acid per ml. To each tube 1 ml. of the hydrochloric acid solution of stannous chloride is added. The tubes are placed in a boiling water-bath for 15 minutes, after which they are removed and cooled. To each tube 2 ml. of glacial acetic acid are added in such a manner that it flows down the sides of the tubes and removes any condensed water. Three ml. of alcoholic aniline solution are now added to the tubes, so that a layer is formed. Finally the contents of the tubes are thoroughly mixed by shaking and then allowed to stand for 10 minutes to allow the maximum colour development, and the unknown is compared in a colorimeter with the standard which most closely matches it. The non-ascorbic acid furfural is estimated by placing 1 ml. of the Norit filtrate in a test-tube of the size previously described, and adding to

each of three similar tubes 1 ml. of the ascorbic acid standards, choosing the equivalents of 0·03, 0·02 and 0·01 mg. of ascorbic acid per ml. To each tube 1 ml. of a 30 per cent. solution of hydrochloric acid is added. The tubes are placed in a boiling water-bath for 15 minutes, after which they are removed and the contents are cooled. To each tube 1 ml. of a freshly prepared 1 per cent. aqueous stannous chloride solution is added, followed by 2 ml. of glacial acetic acid and 3 ml. of alcoholic aniline solution. The contents of the tubes are mixed, and the procedure described above is followed. For vegetable or fruit juices, the juice is diluted to 10 volumes, and, if acid, is treated with excess of solid calcium carbonate. From this point, the procedure is that described for the neutralised oxalic acid extract of tissues. Sometimes 2 hours may be necessary for the completion of the fermentation.

For animal tissues, the material is ground with sand and 6 volumes of a 5 per cent. sulphosalicylic acid solution in 10 per cent. acetic acid. The extract is filtered through gauze, and the residue is washed with similar solution until 10 volumes are obtained. The extract and washings are mixed and centrifuged. To 10 ml. of the clear liquid 0·5 g. of the acid-washed Norit are added, the whole is shaken for 2 minutes and filtered, and from this point the procedure is as described above. Liver tissue is assayed by grinding with the sulphosalicylic-acetic acid mixture followed by the Norit treatment as before. To 5 ml. of the Norit filtrate an equal volume of absolute ethyl alcohol is added to precipitate the glycogen. The solution is mixed and centrifuged. The subsequent procedure is as previously described, except that 2 ml. of the alcoholic filtrate are used and 1 ml. of absolute alcohol is added to each standard tube. Recovery of added ascorbic acid varied from 94 to 100 per cent. This method was compared with the indophenol titration, using Tillman's method but extracting the material with 10 volumes of the sulphosalicylic-acetic acid mixture. Close agreement was obtained between the two methods upon brain, heart, intestine, kidney, spleen, adrenal glands, lens and aqueous tumour of the eye and plant tissues, but with liver the titration method gave results 25 per cent. higher than the colorimetric method. The results indicate that in the plant and animal tissues examined ascorbic acid exists in the reduced form only. S. G. S.

Effect of Light on the Vitamin *C* of Milk. S. K. Kon and M. B. Watson. (*Biochem. J.*, 1936, **30**, 2273–2290.)—Milk which originally gave a positive chemical test for vitamin *C* failed to reduce the indophenol reagent after exposure to daylight through glass. The reducing power was restored to a varying extent by treatment with hydrogen sulphide, but irreversible losses always occurred. Visible light of short wave-length (blue and violet) was chiefly responsible for the reaction, and ultra-violet light was also probably active, but yellow and red light had practically no effect. The presence of oxygen was necessary for the action of light, and the reversible oxidation taking place followed the laws of a unimolecular reaction, having a temperature coefficient of 1·4 for a range of 0° to 37° C. It is probably a chain reaction. The decomposition of the reversibly oxidised ascorbic acid is a more complicated reaction which remains incomplete. It is suggested that the effect of light on the ascorbic acid of milk is a part of the general oxidative changes induced in milk by the actinic activation of oxygen. It is also suggested

that the mechanism of the breakdown of the ascorbic acid is similar to the known oxidation decomposition of this substance, namely, that dehydroascorbic acid is formed in the reversible oxidation, and that the opening of the lactone ring takes place in the course of the further irreversible changes. Synthetic ascorbic acid added to milk, behaves, under the action of light, in the same way as the ascorbic acid originally present. Tests on guinea-pigs confirm the chemical findings. A pint bottle of milk exposed to the sun under conditions likely to occur in practice, on the door-step for half-an-hour, and then kept for 1 hour in the dark, lost half of its original antiscorbutic properties. Milk as secreted by the normal cow contains only reduced ascorbic acid, but when this milk is pasteurised by the holder method, any reversibly oxidised ascorbic acid is destroyed, whilst the reduced form is not affected. In the absence of catalytic metals, the amount of vitamin *C* destroyed by pasteurisation depends on the previous exposure of the milk to light. S. G. S.

Vitamin *C* in Vegetables. Ascorbic Acid Oxidase. Z. I. Kertesz, R. B. Dearborn and G. L. Mack. (*J. Biol. Chem.*, 1936, **116**, 717–725.)—Ascorbic acid oxidase, which has been reported in cabbage and squash, has also been found in many other vegetables, but the relative activity of the enzyme varies greatly in different vegetables. The presence of this enzyme, which is completely inactivated in vegetables or their extracts by heating at 100° C. for 1 minute, is instrumental in the loss of physiologically active forms of ascorbic acid by catalysing the formation of dehydroascorbic acid, which is more readily decomposed by a non-enzyme reaction into a compound having no antiscorbutic activity. Peas frozen after sufficient heat-treatment to inactivate the ascorbic acid oxidase retained a much greater portion of their original ascorbic acid content than those having the active enzyme present. Since the ascorbic acid oxidase and catalase appear to be inactivated by heat at the same rate, the commercial practice of establishing the proper blanching time by a test for catalase activity also yields information on the inactivation of the ascorbic acid oxidase. S. G. S.

Bacteriological

Parachlorometaxylenol as a Preservative. E. A. Lam. (*Pharm. J.*, 1937, **138**, 76.)—The chlorinated xylenols are being increasingly used as non-poisonous antiseptics and disinfectants in saponaceous solution, but there does not appear to have been any published information about their use as preservatives for bacterial preparations such as vaccines. Parachlorometaxylenol (1-hydroxy-3 : 5-dimethyl-4-chlorobenzene) is a white crystalline powder with a phenolic odour which in a saponaceous solvent has a Rideal–Walker coefficient of about 60 (*Pharm. J.*, 1936, **197**, 273), and in 3 per cent. saponaceous solution a coefficient of 1·6. Phenol and cresols, which are normally used for the preservation of vaccines, have been criticised because of their inefficiency.

An experiment is recorded on the use of 0·5 per cent. phenol together with 0·035 per cent. parachlormetaxylenol as an antiseptic in a vaccine containing Pfeiffer's bacillus, Friedländer's bacillus, streptococci, staphylococci and *B. septus*,

and on the use of 0·5 per cent. phenol alone for the same vaccine. Five ml. of each were exposed to a dusty atmosphere for periods of ½ hour, 1 hour and 12 hours. The former was sterile after 12 hours, the latter after ½ hour, and showed scanty growth of staphylococci after 1 hour, and heavy growth of staphylococci and other micro-organisms after 12 hours. This experiment demonstrates the enhanced antiseptic effect obtained by the addition of a small quantity of parachlorometa-xylenol, and suggests that it is worthy of further trial in vaccines and other bacteriological products. D. R. W.

Toxicological

Toxicological Detection of Zinc Phosphide. F. Haun. (*Z. Unters. Lebensm.*, 1936, **72**, 307–312.)—Zinc phosphide has recently been employed as a means of combating domestic and agricultural pests, such as rats, mice and crows, and a number of preparations for this purpose are on the market. The commercial phosphide occurs as a grey, sintered mass, stable in air and transformed by heat into zinc phosphate. It is insoluble in water. By the action of dilute mineral acids or acetic acid upon it, phosphine is liberated, and cold conc. nitric acid decomposes it with explosive violence. A sample contained 19·17 per cent. of phosphorus and 71·03 per cent. of zinc, but, as this composition does not correspond with the composition of any one of the known pure phosphides of zinc, it is probable that a portion of the zinc is present as oxide or phosphate, or that the substance is a mixture of the different phosphides of zinc. The substance is used mixed with cattle food, especially with wheat, bran or carob bean. Occasionally, it is mixed with meat with which "blown" eggs are filled to serve as a bait for crows. The wheat product is sometimes coloured red, but when unstained it has a black, corroded appearance. For white mice one grain of the wheat preparation was found to be insufficient, but two grains caused death within twenty-four hours. With birds no specific indication of its presence appeared in the crop, but on dissecting the carcase, the odour of phosphine was usually apparent. This odour, occurring in the stomach, affords a strong presumption that death is due to zinc phosphide poisoning, and with a little experience the odour is readily distinguished from that of arsine. The pharynx is usually inflamed and red. The stomach and intestines are inflamed and suffused with blood. There is inflammation of the kidneys and the liver is swollen and yellow. If the material is not highly decomposed, phosphine can be detected. If decomposition has reached an advanced stage, proof of the presence of zinc phosphide must depend upon the detection of zinc and a consideration of the symptoms. The amount of zinc found in the investigations undertaken was so small that poisoning by other zinc salts was excluded. The simplest and most rapid method for the detection of phosphine is as follows:—A few grams (5 to 10 are sufficient or, if a negative result is expected, 20 to 30 g.) are placed in a small (50 or 100 ml.) flask. Dilute sulphuric acid containing a little copper or cadmium salt is then added, and the flask is immediately closed by means of a cork stopper carrying a mercuric bromide paper. After a short time the paper is stained yellow by the phosphine evolved. Mercuric cadmium iodide paper moistened with a drop of acetic anhydride may also be used

and, since the presence of hydrogen sulphide does not affect this test, the dilute sulphuric acid used needs no addition. The papers must be freshly prepared, that of mercuric bromide from a 5 per cent. alcoholic solution and that of mercury cadmium iodide from a 5 per cent. aqueous solution (Weber, *Arb. Reichs-Gesund-Amt*, 1934, **67**, 183). Methods depending upon the isolation of phosphine by distillation are not recommended owing to their liability to cause explosions. Detection of zinc by precipitation as sulphide from large amounts of material is tedious. Detection by means of dithizone or by Rinmann's green is also not satisfactory. Detection with ferrocyanide involves the separation of iron and the test is not specific in the presence of manganese. Detection by means of cobalt mercury thiocyanate provides a rapid and convenient method. The reagents required are:—Cobalt sulphate solution (0·095 g. of $CoSO_4 \cdot 7H_2O$ in 100 ml. of *N*/2 hydrochloric acid), alkali mercury thiocyanate solution (8 g. of mercuric chloride and 9 g. of ammonium thiocyanate in 100 ml. of water, allowed to stand for a few days) and solid alkali fluoride. A portion of the material (5 to 10 g., or 20 to 30 g. if a negative result is expected), is mixed with some sodium carbonate and ignited. The residue is acidified with hydrochloric acid, and the solution is evaporated to a small bulk and poured off from any large amount of sodium chloride which separates. The solution to be tested must be neutral or only faintly acid. One or two drops of the solution are mixed with one or two drops each of the mercury and double thiocyanate cobalt solutions in the depression of a porcelain tile. If a red colour (due to iron) develops in one or two minutes, a milligram of solid alkali fluoride is added and will cause its disappearance. The mixture is then stirred, and the sides of the vessel are rubbed with a glass rod for 15 seconds. Immediately, or in not more than two minutes, a blue precipitate forms. Subsequent formation of a blue colour is not specific for zinc. A control experiment should be carried out with a drop of pure water. The cobalt solution will give a blue colour when allowed to stand for a long time after addition of the mercury thiocyanate solution, but this colour appears immediately in the presence of very small amounts of zinc.

A. O. J.

Agricultural

Cacao Shell and Its Use as an Accessory Fodder. A. W. Knapp and A. Churchman. (*Chem. and Ind.*, 1937, **56**, 29–33.)—The present paper brings previous work up to date (*cf.* ANALYST, 1919, **44**, 2; *J. Soc. Chem. Ind.*, 1918, **37**, 240). In 1935 the total available cacao shell, based on the yield of 10·5 lb. from 100 lb. of beans, is estimated at 65,000 tons, of which 8,000 tons were produced in Great Britain. Analysis of five commercial samples of large shell gave the following results:

	1	2	3	4	5
Moisture, per cent.	4·6	6·7	7·8	7·0	10·9
Petroleum spirit extract, per cent.	3·0	3·1	2·5	4·3	4·2
Zeiss refractometer reading of fat at 40° C.	57	61	57	56	63
Ash, per cent.	12·4	8·4	7·9	7·3	9·0
Theobromine on dry shell, per cent.	1·26	1·55	1·69	0·80	0·98

The fuel value of the shell is about 8000 B.Th.U. The gas obtained is equivalent in power to ordinary producer gas, but the main uses of the shell are as an ingredient in cattle food and, to a less extent, as a fertiliser. It should not be used as a cheap innocuous filler or appetiser in cattle food, but with due regard to its peculiar properties. The complete analysis of a commercial roasted large shell is as follows in percentages:—Water, 3·8; fat, 3·4. Ash: total, 8·1; water-soluble, 3·5; water-insoluble, 4·6; silica (*i.e.* acid-insoluble), 1·1; alkalinity (as K_2O), 2·6; chlorides (as salt), 0·07; iron (Fe_2O_3), 0·03; phosphoric acid (P_2O_5), 0·8; copper, 0·004. Nitrogen: total nitrogen, 2·8; protein nitrogen, 2·1; ammoniacal, 0·04; amide nitrogen, 0·1; theobromine, 1·3; caffeine, 0·1. Carbohydrates: sucrose, nil; glucose, 0·1; starch (by takadiastase method), 2·8 (no true starch); pectins, 8·0; fibre, 18·6; cellulose, 13·7; pentosans, 7·1; mucilage, 9·0. Tannins: acetone-soluble, 1·8; tannic acid (Löwenthal), 1·3; cocoa red, 2·0. Acids: acetic (free), 0·1; citric, 0·7; oxalic, 0·32. Extracts: cold water, 20·0; alcohol, 10·0. A general analysis of cacao shell compared with meadow hay is as follows:

	Cacao shell Per Cent.	Meadow hay Per Cent.
Dry matter	95·45	84·0
Protein	16·07	13·5
Fat	4·62	3·0
Carbohydrates	47·56	40·5
Crude fibre	18·23	19·3
Mineral salts	7·92	7·7
Theobromine	1·03	—

Following the experimental feeding experiments carried on at Reading University and the satisfactory results obtained therefrom, the shell has now been fed to two herds of cows (28 and 25 head) producing Grade A milk, 2 lb. per day being given to each cow for a period of approximately 7 months from October 4th, and continued after the cows were out at grass. The cows all showed a liking for the shell, no scouring occurred—in fact rather the reverse—and the shell was found to store satisfactorily. As with the Reading tests, there was a distinct tendency to an increase in butter-fat in the milk, and this was noticeable when comparing with results on the control farms. Also cacao shell has a high vitamin *D* potency (ANALYST, 1936, **61**, 350), at least a quarter that of cod-liver oil. The importance of keeping to a 2-lb. ration is emphasised, since the theobromine is a stimulant. This quantity enables the farmer to obtain full value from the digestible constituents of the shell. D. G. H.

Organic

Rapid Qualitative Detection of Nitrogen in Organic Substances. H. Gauduchon-Truchot. (*Ann. Chim. anal.*, 1936, **18**, 316–317.)—To a little of the substance contained in a test-tube is added 1 ml. of pure sulphuric acid. The liquid is heated to boiling and dilute perchloric acid (66 per cent. perchloric acid diluted to one-third strength) is added, drop by drop, until decolorisation occurs. The tube is then cooled in running water, an excess of sodium hydroxide solution is added, and ammonia is tested for by litmus paper or paper saturated with Nessler reagent placed in the mouth of the tube. In tests with pyramidon only

a few minutes' heating with the sulphuric-perchloric acid mixture were required for decolorisation, which was quicker by the use of the dilute than with strong perchloric acid. Positive tests for nitrogen were obtained with a wide range of organic nitrogenous compounds. S. G. C.

Determination of Nitrogen in Kuznetzky Basin Coals by Formol Titration. T. M. Slobodskaya. (*Zavodskaya Laboratoriya*, 1936, 600–601.)—Coal is decomposed by the Kjeldahl process, the residue is transferred to a conical flask, diluted with water to 150 ml., roughly neutralised in presence of methyl red, with 30 per cent. sodium hydroxide solution, and, after removal of carbon dioxide by boiling, neutralised accurately with $N/10$ and acidified with 3 drops of $N/10$ sulphuric acid. Twenty ml. of formalin neutralised to phenolphthalein are added, and the liquid is titrated with $N/10$ sodium hydroxide solution. The number of ml. of sodium hydroxide solution, multiplied by 0·0014, gives the weight of nitrogen in the sample. The reaction is expressed by the following equation:—

$$2(NH_4)_2SO_4 + 6HCHO = (CH_2)_6N_4 + 6H_2O + 2H_2SO_4$$ S. P. S.

The Triene Acid from Seeds of Pomegranates. E. H. Farmer and F. A. Van den Heuvel. (*J. Chem. Soc.*, 1936, 1809–1811.)—Punicic acid was extracted from seeds of pomegranate by disintegrating the seeds in a mincing machine, extracting with ether, evaporating off the solvent, saponifying the fat with alcoholic potash, and converting the liberated fatty acids into their magnesium salts, as described by Toyama and Tsuchiya (*J. Soc. Chem. Ind., Japan*, 1935, **38**, 182B, 185B; Abst., ANALYST, 1935, **60**, 570). The portion of the magnesium salts most soluble in alcohol yielded a solid acid which, after two re-crystallisations from 80 per cent. alcohol and one from petroleum spirit (b.p. 60°–80° C.), followed by thorough drying, melted at 44° C. It contained carbon, 77·25 per cent., and hydrogen, 10·5 per cent., the calculated figures for the acid $C_{18}H_{30}O_2$ being 77·6 per cent. and 10·85 per cent., respectively. The acid had neutralisation value 201·0 (calculated for elaeostearic acid, 201·7), and iodine value (Wijs), 217·5 (calculated, 273·7). It yielded no maleic anhydride derivative, and was converted into β-elaeostearic acid by exposing it in 10 per cent. solution in xylene, in contact with a little sulphur and in an atmosphere of nitrogen, for 4 hours to the light from a mercury-vapour lamp. The acid was hydrogenated to stearic acid, and on oxidation with permanganate yielded a mixture of azelaic acid, oxalic acid, and valeric acid. With α-elaeostearic acid it gave a eutectic point of 35° C., and with β-elaeostearic acid a eutectic point of 38° C. The claim of the Japanese authors (*loc. cit.*) to have isolated a third (doubtlessly geometrically isomeric) form of elaeostearic acid is therefore substantiated. E. M. P.

Determination of Hydroxylated Acids of Fats. P. G. Hofner, R. H. Swinney and E. S. West. (*J. Biol. Chem.*, 1936, **116**, 691–697.)—Samples for analysis are weighed into two dry reaction tubes (0·5 to 1·0 g. of materials with high acetyl values and 1·0 to 1·5 g. of those with low values). In one tube are placed 5·0 ml. of the acetylating mixture, and in the other 5·0 ml. of pyridine. A third tube is charged accurately with 5·0 ml. of the acetylating mixture alone. The

condensers, carefully filled with water and dry on the outside, are suspended in the reaction tubes, which are then placed in the holes of the steam-bath and heated for 1¼ hours. The condensers are then slightly raised, and 5 ml. of water are added to each reaction tube; the condensers are replaced and the tubes are heated 15 minutes longer, with occasional careful shaking. After cooling, the condensers and the reaction tubes are rinsed down with 15 ml. of butyl alcohol, and the solutions are titrated with the alcoholic alkali, 4 drops of 1 per cent. phenolphthalein solution being used as indicator. The titrations of duplicate blanks should not vary more than 0·02 ml., the end-points being very sharp. Calculations, as mg. of acetyl found per g. of sample, are based on the method of West, Hoagland and Curtis (*J. Biol. Chem.*, 1934, **104**, 627). The acetic anhydride, pyridine and butyl alcohol are as previously used by these latter authors. The alcoholic alkali is 0·5 *N* potassium hydroxide, aldehyde-free, and is prepared according to the method of Malfatti (*Z. anal. Chem.*, 1912, **50**, 692). The acetylating mixture consists of one volume of acetic anhydride and seven volumes of pyridine. The reaction tubes are (25 × 200 mm.) Pyrex test-tubes; the condenser tubes are (18 × 150 mm.) Pyrex tubes with a rubber ring under the rim. The cover of the steam-bath is made of heavy sheet metal or painted re-inforced board, and the holes are 1⅛ in. in diameter. Rubber rings are fitted near the bottoms of the reaction tubes, so that they may be placed through the holes in the steam-bath cover with the bottoms of the tubes projecting 5 cm. below the cover into the bath. The pipettes are those described by West, *et al.* A 25-ml. burette graduated in 0·05 ml. with a 20-gauge stainless hypodermic needle fitted to the tip is employed. This tip delivers 0·007 ml. of 0·5 *N* potassium hydroxide solution per drop. The authors used the titration apparatus described by West (*Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 62), but a hand stirrer, consisting of a small glass rod with a loop or coil at the bottom and bent at right angles to the stem, may also be used. S. G. S.

Seed Wax of *Simmondsia californica*. T. G. Green, T. P. Hilditch and W. J. Stainsby. (*J. Chem. Soc.*, 1936, 1750–1755.)—The work of Greene and Foster (*Bot. Gazette*, 1933, **94**, 826) on the liquid oil obtained from seeds of *Simmondsia californica* Nutt. has been extended. A golden-yellow oil, with saponification equivalent 604·1 and iodine value 86·3, was extracted with light petroleum (b.p. 40°–60° C.) from ground-up seed kernels. The oil was hydrolysed with an excess of alcoholic potassium hydroxide, the alcohols were separated from the solution of potassium soaps, and the acids were recovered and re-saponified in order to ensure complete hydrolysis of the wax. There were obtained 95·6 g. of acids (mean molec. equiv., 309·6; iodine value, 82·1) and 91·9 g. of alcohols (mean molec. equiv., 307·7; iodine value, 84·3). The acids were converted into their lead salts, the latter were separated into soluble and insoluble salts, and the methyl esters of the two groups of acids were fractionally distilled *in vacuo*. The two groups of acids were, for the most part, similar, except that the acids with soluble lead salts appeared to contain minor quantities (not more than 6 to 7 per cent. of the total acids) of oleic and palmitic acids. The constants of the methyl esters are given in tables. The chief acid present was identified as $\Delta^{11:12}$-eicosenoic acid, accompanied by smaller quantities of a higher (possibly docosenoic) acid.

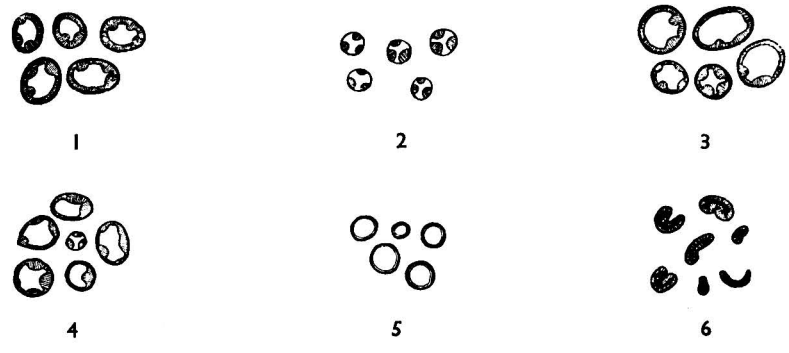
The mixed alcohols were also fractionally distilled *in vacuo* and studied by hydrogenation and oxidation to acids and to trihydric alcohols. The results indicated that $\Delta^{13:14}$-docosenol is present, and that the other alcohol, which is present in equal or slightly larger proportion, is probably $\Delta^{11:12}$-eicosenol. E. M. P.

Determination of Thiourea. R. Cuthill and C. Atkins. (*J. Soc. Chem. Ind.*, **1937**, **56**, 5–8T.)—The reaction of thiourea with silver nitrate and with various oxidising agents has been examined with a view to their utilisation in studying the sorption of thiourea from aqueous solution. In Volhard's method (addition of silver nitrate to the ammoniacal solution) the end-point cannot be precisely located, and the method was improved by adding excess of standard silver nitrate and, after reaction had occurred, acidifying with nitric acid, filtering off the precipitate, and determining the excess of silver in the filtrate by titration with standard thiocyanate. It was found that the amount of ammonia may vary within wide limits provided the amount of free acid finally present does not vary greatly. The concentration of nitric acid, other conditions remaining the same, could be varied between 2 *N* and 8 *N* without affecting the accuracy of the result, and the method was found equally accurate for all concentrations of thiourea between 0·5 and 5·25 g. per litre. Various oxidising agents were also tried. Neither potassium permanganate nor chloramine T was satisfactory. With ceric sulphate the following procedure gave good results (*cf.* ANALYST, 1928, **53**, 404):—A mixture of 10 ml. of approximately 0·025 *N* thiourea solution, 25 ml. of 0·1 *N* ceric sulphate solution and 25 ml. of 4 *N* sulphuric acid are boiled under a reflux condenser for 30 minutes and, after cooling, the excess of ceric sulphate is titrated with 0·025 *N* ferrous ammonium sulphate solution, with the use of xylene-cyanol FF as indicator (not all preparations on the market appear to be suitable). When the concentration of thiourea falls below about 1 g. per litre, oxidation appears not to be complete. Potassium dichromate may be used as the oxidising agent under almost the same conditions as ceric acid, and recovery was 100·8 per cent. with as small a quantity of thiourea as 0·1691 g. per litre. If iodine in alkaline solution is used, 10 ml. of approximately 0·025 *M* thiourea solution are mixed with 10 ml. of 2 *N* sodium hydroxide solution, then 50 ml. of 0·1 *N* iodine solution are added, and after 15 minutes the mixture is acidified with 20 ml. of 4 *N* sulphuric acid and titrated with 0·1 *N* sodium thiosulphate solution. Four mols. of iodine react with 1 mol. of thiourea. The method was accurate for concentrations of thiourea between 3·19 and 0·1595 g. per litre. D. G. H.

Analysis of Tanning Materials by the Use of Dry Chromed Hide Powders. J. G. Parker and A. Harvey. (*J. Int. Soc. Leather Trades Chem.*, 1936, **20**, 545–550.)—A historical survey is given of the controversy over Baldracco and Camilla's modification (*id.*, 1919, **3**, 111; 1920, **4**, 88; 1929, **13**, 365; 1935, **19**, 367) of the official "Shake Method," from which it is concluded that a dry chromed powder of standard quality giving results in accordance with the official method is commercially available, and that the proposed method is simpler, more rapid and less subject to errors. The authors therefore decided to test the effect of age on Lyons, Freiberg and Turin hide powders, which had been stored in unsealed tins, using the Baldracco method as provisionally approved, as follows:—The dry

ready-chromed hide powder (6·5 g.) is shaken in the improved Darmstadt apparatus (*cf.* Parker, *id.*, 1928, **12**, 520) with 75 ml. of the tannin solution to be analysed, for 15 minutes, in a mechanical shaker rotating at 50 to 60 r.p.m. The partially detanninised solution is separated with the aid of a vacuum pump, and the procedure is repeated on a further 75 ml. of tannin solution, with shaking for 20 minutes. The detanninised solution is then collected in a dry beaker, 50 ml. are evaporated to dryness, and the residue is weighed. The Darmstadt apparatus consists of a glass crucible to which a cap may be attached by springs, so that the liquid it contains may be shaken and subsequently filtered by attaching the crucible to a filter-flask. Comparisons of the results obtained (in 42 tests with 15 different tanning agents) for the above-mentioned three hide powders and by the official method showed that dry pre-chromed hide powders give results in agreement with those obtained by the official method, even if the powders have been stored for 3 to 6 years and are derived from different sources (*cf.* Stather, *id.*, 1935, **19**, 370). J. G.

Recognition of Akon- (Akund-) Vessels in Kapok. N. J. M. Vorstman. (*Chem. Weekblad*, 1936, **33**, 746–747.)—The conclusions of Dingemans (*id.*, 1936, **33**, 8) are criticised. Thus, the colour-reaction with a solution of phloroglucinol in hydrochloric acid is unreliable, because a sample of genuine Java kapok gave such a strong red colour that it might easily have been mistaken for akon, whilst



(1) Bombay akon (*Calotropis procera*). (2) Widoeri (*Calotropis gigantea*). (3) Commercial "kapok" (akon). (4) Commercial akon (widoeri admixture). (5) Kapok. (6) Katoen (cotton).

different types of akon gave colours of varying intensity which were so weak in some cases as to be misleading. The safranine and neocarmine stains were even less satisfactory. The longitudinal markings, which are characteristic of akon, may be rendered visible under the microscope by racking the objective up and down. According to Dingemans, the single hairs are usually silky with thin walls, and there are 2 to 5 longitudinal markings with reticular cross-connections. The influence on this test of the presence of an air-bell is discussed, and in this connection cross-sections of the vessels were cut from samples of the fibres embedded in collodion. Figs. 1 to 6 show, respectively, Bombay akon (*Calotropis procera*), Widoeri (*C. gigantea*), a commercial sample alleged to be kapok but really akon, commercial akon (containing Widoeri), genuine kapok, and cotton (for comparison,

as no lumen is visible). The circular section and uniformly thin walls are characteristic of all types of kapok, and the longitudinal markings of akon are plainly visible as 2 to 4 irregularities in thickness in the walls; these are frequently spaced at regular intervals around the periphery (*cf.* Hansma, *id.*, 1936, **33**, 620, 624).

J. G.

Inorganic

Detection of Manganese. N. A. Tananaeff. (*Z. anal. Chem.*, 1936, **107**, 343–347.)—The solution to be tested (2 to 3 ml.) is neutralised with alkali hydroxide until slightly cloudy, and treated with a moderate excess of potassium cyanide. The cyanides of a number of metals re-dissolve, whilst the hydroxides of aluminium, chromium, lead, and bismuth are precipitated. Sodium peroxide in small portions is added to the solution, which is heated to boiling; aluminium, chromium, and lead dissolve, whilst manganese dioxide is precipitated. Bismuth hydroxide remains insoluble, but does not vitiate the test. If bismuth preponderates, the cyanide solution may be filtered prior to treatment with peroxide. Steels and cast iron are dissolved in nitric acid, the iron is precipitated with zinc oxide, the solution is boiled and filtered, and the filtrate is tested as described above. The test detects 0·0001 g. of manganese in 4 ml. of solution. W. R. S.

Colorimetric Determination of Titanium in Presence of Bromide. D. Lewis. (*Z. anal. Chem.*, 1936, **107**, 408–409.)—Bromide is oxidised in acid solution by hydrogen peroxide, whereby the solution becomes coloured; hence bromide interferes in the colorimetric determination of titanium. The interference can be overcome without additional manipulation by treatment of the solution with acetone, a colourless bromine substitution product being formed. The solution to be tested is treated with 30 ml. of 12 *N* sulphuric acid, 3 ml. of 3 per cent. hydrogen peroxide and 5 ml. of pure acetone, and diluted to 100 ml. The colorimetric determination is then carried out as usual. W. R. S.

Determination of Potassium as Cobaltinitrite. L. Jendrassik and A. Polgár. (*Z. anal. Chem.*, 1936, **107**, 417–420.)—The authors find the cobaltinitrite method to give accurate results provided that the precipitation is carried out as described, not with a stock solution of the precipitant. The precipitate is dissolved in strong sulphuric acid, and the nitrite is determined volumetrically. The solution (10 ml., containing 0·002 to 0·01 g. of potassium) is treated with 5 ml. of 25 per cent. cobalt sulphate or nitrate solution, 10 ml. of 50 per cent. sodium nitrite solution, and 5 ml. of acetate mixture (2 parts of strong sodium acetate solution to 1 part of acetic acid). Two blank tests are made with 10 ml. of water. The beakers are left in the cold for 5 to 18 hours, and the precipitates are collected under gentle suction on asbestos supported by a perforated porcelain plate. The asbestos filter should be purified before use by successive treatments with water, 10 ml. of strong sulphuric acid, 10 to 30 ml. of 0·005 *N* permanganate solution, the same quantity of *N* sodium hydroxide solution, and finally with water. Precipitate and beaker are washed with 50 to 70 ml. of water. The funnel is then transferred to another suction flask containing 200 ml. of water

and 20 ml. of 0·1 *N* permanganate solution. Strong sulphuric acid (10 ml.) is added to the funnel, and 3 ml. to the precipitation beaker. When the precipitate has dissolved, the acid is drawn into the suction flask. The filter is washed with the 3 ml. of acid from the beaker, then twice with 3 ml. of 50 per cent. sulphuric acid, and then with water. The permanganate solution is left to cool for a few minutes, treated with 5 ml. of 15 per cent. potassium iodide solution, and titrated with 0·1 *N* thiosulphate. The blanks are treated in the same manner, the asbestos filter being available for use again after an intervening treatment with acid permanganate solution, caustic alkali, and water. The difference between the blank reading and the assay is multiplied by 0·6515 (the stoichiometric factor for potassium), giving the quantity in mg. The mean error in 22 determinations of 0·008 g. of potassium was 0·02 per cent. With 0·002 to 0·004 g. of metal the error did not reach 0·3 per cent. W. R. S.

Determination of Small Quantities of Hydrogen Sulphide and Sulphur Dioxide. W. G. Gurevitch and W. P. Wendt. (*J. Obshchei Chimii*, 1936, **6**, 962–971.)—It is shown that the oxidation of sulphites by air in ammoniacal solution is accelerated in presence of copper compounds and still more so by cobalt salts, which are nine times as active as copper salts; hydrogen sulphide, on the other hand, is little affected during the 30 minutes' period of the test. By adding lead nitrate to the acidified solution in dilute alcohol, the resulting turbidity, due to lead sulphate, is much more stable than a barium sulphate turbidity. The intensity of the turbidity is measured by means of a nephelometer, the construction of which is described. The sulphur dioxide and hydrogen sulphide are oxidised together by means of hydrogen peroxide, and the sulphuric acid produced is determined by the same turbidity method. S. P. S.

Sodium Chlorite as a Volumetric Oxidising Agent. D. T. Jackson and J. L. Parsons. (*Ind. Eng. Chem. Anal., Ed.*, 1937, **9**, 14–15.)—Sodium chlorite is now available commercially as a white finely crystalline powder which is slightly hygroscopic. Its solubility is 91·3 parts in 100 parts of water at 30° C. The freshly-prepared solution is colourless, but, when exposed to light, it gradually changes to yellowish-green, and loses oxidising power. The solution was found to be entirely stable, however, if kept in a glass-stoppered bottle and protected from light. The reagent is proposed for the determination of sulphite. To the sulphite solution (100 ml.), 15 ml. of 10 per cent. potassium iodide solution, 15 ml. of 30 per cent. acetic acid and 5 ml. of 1 per cent. starch solution are added. The liquid is titrated with standard chlorite solution to the appearance of a permanent starch-iodine blue colour. A *N*/10 solution (which contains one-fortieth of the gram-molecular weight) may be standardised by addition of potassium iodide and dilute acetic acid and titration with standard thiosulphate. S. G. C.

Explosion Risks in the Use of Perchloric Acid. (*a*) **O. Hackl** (*Z. anal. Chem.*, 1936, **107**, 385–387), (*b*) **J. Meyer and W. Spormann** (*ibid.*, 387–388.)—(*a*) Extracts from the American literature are given on the danger of explosions in evaporating, boiling, or distilling perchloric acid in presence of organic matter,

e.g. alcohols, rubber-stoppers, or other oxidisable substances such as antimony trioxide. The passages quoted occur in Hillebrand and Lundell's *Applied Inorganic Analysis* (p. 37), Noyes and Bray's *System of Qualitative Analysis for the Rarer Elements* (pp. 32, 286), and Washington's *Chemical Analysis of Rocks* (4th Ed., pp. 236, 237). The author has used the perchlorate method for the determination of potassium in rocks and mineral waters for many years without experiencing any explosions, because he never heated or evaporated the alcoholic filtrates.

(*b*) The formation of very explosive perchloric esters has been advanced as the cause of explosions in the evaporation of alcoholic solutions of perchloric acid, but such ester formation is possible only in the absence of water. The explosions must be due to spontaneous decomposition of the acid in contact with oxidisable substances, though the mechanism of the reaction is still obscure. Whatever the cause, the evaporation of such alcoholic solutions should be avoided. Aqueous solutions of perchloric acid can be evaporated with impunity. (*Cf.* ANALYST, **1931**, **56**, 686.) W. R. S.

Detection of Traces of Sulphur in Argon. I. I. Strishevsky and I. V. Korablev. (*Zavodskaya Laboratoriya*, 1936, 591–592.)—Advantage is taken of the following reactions:

1. $S + H_2 = H_2S$
2. $SO_2 + 3H_2 = H_2S + 2H_2O$
3. $SO_3 + 4H_2 = H_2S + 3H_2O$

Argon and hydrogen are passed through a Y-piece into a glass tube in which is fused a platinum capillary heated to 800° C. in an electric furnace. The gas is then conducted into an inverted funnel dipping in a 10 per cent. lead acetate solution. S. P. S.

Volumetric Determination of Selenic Acid. R. Dolique. (*Ann. Chim. Anal.*, 1936, **18**, 313–315.)—The solution (100 ml.), containing about 40 ml. of conc. hydrochloric acid (sp.gr. 1·19) for each 0·2 g. of selenic acid present, is heated nearly to boiling for 10 minutes in a flask fitted with a reflux condenser. During this time a slow stream of carbon dioxide is passed through the apparatus, the chlorine, liberated according to the reaction,

$$H_2SeO_4 + 2HCl \rightleftharpoons H_2SeO_3 + H_2O + Cl_2$$

which proceeds practically to completion, is received in potassium iodide solution, and the liberated iodine is titrated with standard thiosulphate solution. The precision of the method is stated to be about 0·5 per cent. S. G. C.

Microchemical

Spot Tests for Substances Sparingly Soluble in Acids. F. Feigl. (*Mikrochem.*, 1936, **20**, 198–208.)—Certain constituents of the insoluble residue may readily be identified: (1) *Insoluble sulphide*, such as mercuric sulphide, arsenic sulphide and naturally occurring sulphides, *e.g.* pyrites. The sulphide may be detected by catalysis of the iodine-azide reaction:—$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$. A few granules of the sample are placed on a watch-glass and covered with 1 or 2 drops of the reagent (3 g. of sodium azide in 100 ml. of 0·1 *N* iodine solution), and

the occurrence of bubbles of nitrogen is noted. (2) *Insoluble sulphate*, such as lead sulphate, barium sulphate, strontium sulphate and calcium sulphate:—When sulphides and free sulphur are absent the sample is reduced to potassium sulphide with metallic potassium and identified by means of the azide-iodine reaction or the sodium nitroprusside test. The reduction is carried out in a small hard glass tube with a bulb. The potassium is carefully melted, the tube is heated to redness for a short time, and then broken by placing it in about 5 drops of water, The test for sulphide is carried out on the extract without filtering. Lead sulphate can be detected in the presence of the alkaline earth sulphates by stirring about 1 mg. of the sample with a warm mixture of acetic acid and ammonium acetate, which dissolves the lead as a complex acetate. The suspension is taken up on filter-paper, treated with hydrogen sulphide, when a black stain indicates lead sulphide. (3) *Silver salts*, such as silver iodide, bromide, chloride, cyanide, and thiocyanate: The test depends on the solubility of silver halides in alkali cyanides, with the formation of complex cyanides. A bright red colour or precipitate appears within half-a-minute when the insoluble sample is treated on a white spot-plate with 1 or 2 drops of the reagent prepared from freshly-precipitated and washed nickel cyanide by boiling with potassium cyanide solution in insufficient quantity to dissolve the precipitate, and filtering. This reagent, $K_2[Ni(CN)_4]$, will keep; a few ml. are mixed with a few drops of ammonia and of a saturated alcoholic solution of dimethylglyoxime immediately before the test. Silver iodide may be identified by its reaction with palladous chloride; on steaming the sample on filter-paper treated with a 1 per cent. solution of palladous chloride, a black stain is formed. (4) *Ferric oxide*:—A few grains of the sample are gently warmed with a sulphuric acid solution of potassium or ammonium thiocyanate; the characteristic blood-red colour appears. (5) *Aluminium oxide* must first be taken up by heating with alkali pyrosulphate or bisulphate. Other metals are removed from the aqueous solution by treatment with excess of alkali and centrifuging. The aluminium is then identified by the morin test or the alizarin test. (6) *Chromic oxide and anhydrous chromic chloride*:—The sample is fused with a 1:1 mixture of sodium carbonate and sodium peroxide, dissolved in a few drops of concentrated sulphuric acid, and tested with diphenylcarbazide. Spot tests may also be used to detect the following: manganese dioxide and lead peroxide, after being taken up with dilute nitric acid and hydrogen peroxide; tungstic oxide after fusion with sodium peroxide; metallic tungsten and molybdenum, after fusion with potassium nitrite; silica and silicates, after fusion with sodium potassium carbonate; antimony pentoxide; insoluble fluorides; metastannic acid and stannic phosphate, by a flame test after reduction with zinc and hydrochloric acid (Meissner, ANALYST, 1930, **60**, 465). J. W. M.

Micro-estimation of Menthol, Menthone and Menthyl-esters in the Essential Oils of *Mentha*. H. Ullrich and M. Schneider. (*Hoppe-Seyler's Z. phys. Chem.*, 1936, **245**, 181–184.)—The oil is obtained from the plant or drug by steam distillation in Clavenger's apparatus in a paraffin bath at 130°–140°. The time of distillation varies from 45 to 60 minutes according to the amount of material used. The original apparatus has been modified to include a micro-

burette, having a scale divided to 0·001 ml., below the usual micro-burette. At the end of the distillation the apparatus is allowed to cool and, by running off the water slowly, the oil is transferred to the micro-burette and its volume ascertained. Although there is practically no loss, a correction may be necessary, and this is easily determined. The use of this method necessitates only 1 or 2 g. of material and the accuracy is equal to that with much greater amounts of material. The assay of menthol and menthone by determination of their redox potential is only applicable to chemically pure substances, as other compounds present in the oil have their own effect on the electrodes. In the determination of menthone, the hydroxylamine method of Bennett and Salamon (ANALYST, 1927, **52**, 693) is combined with Rehberg's micro-titration method (*Biochem. J.*, 1925, **19**, 270), and 0·1 *N* alcoholic potassium hydroxide is used instead of the usual 0·5 *N* solution. Menthol is oxidised to menthone with chrom-sulphuric acid, as described by Beckmann (*Annalen*, 1888, **250**, 324), and is then determined by the hydroxylamine method. For the determination of the menthyl esters, the oil is saponified on a water-bath, in a 25-ml. flask connected by a ground-glass joint with an air-condenser. The excess potassium hydroxide is titrated with 0·1 *N* sulphuric acid solution, and the amount used up is calculated to menthyl esters. Hence in an assay of peppermint oil, the menthone is determined direct as such, the menthol is oxidised to menthone which is again determined, and the ester-content is obtained by saponification. S. G. S.

Determination of Small Quantities of Nicotine by a Silicotungstic Acid Micro-method. J. R. Spies. (*Ind. Eng. Chem. Anal. Ed.*, 1937, **9**, 46–47.)—Nicotine in hydrochloric acid solution was determined thus:—A measured volume of the solution of nicotine in *N*/10 hydrochloric acid is placed in a weighed porcelain crucible with darkened interior, and an Emich filter-stick is used (*cf.* Emich, *Microchemical Laboratory Manual*). After dilution to an acidity of *N*/20, the solution is made up to 10 ml. with *N*/20 hydrochloric acid, and stirred with a short 2-mm. glass stirring rod while 0·1 ml. of a 12 per cent. solution of silicotungstic acid is added. (To precipitate 0·5 mg. of nicotine, 0·2 ml. of silicotungstic acid are added.) The stirring rod is then removed and washed with a few drops of 0·005 *N* hydrochloric acid. This rod should be cleaned with warm chromic acid each day before use. The crucibles are covered and allowed to stand overnight, so that the amorphous precipitate may crystallise. The liquid is filtered from the precipitate by means of the filter-stick, and the walls of the crucible and filter-stick are washed three times with approximately 1 to 2 ml. of cold *N*/200 hydrochloric acid. Before ignition the crucibles and filter-stick are dried at 95° to 100° C. to remove excess of water, and then ignited in larger crucibles for 30 minutes in an electric muffle at 650° C., cooled for 2 hours in a desiccator without drying agent, allowed to stand for one hour on a metal block within the outer case of a Kuhlmann microchemical balance, and finally weighed after standing for 5 minutes on the balance pans. After weighing they are ready for another test, without removal of the residue, but it is essential to remove all loosely adhering particles from the filter-stick by tapping it against the crucible wall before removal. Platinum-tipped forceps are always used for holding the crucible. Since the

crucibles are weighed on different days, the usual glass lead-shot counterpoises are replaced by counterpoises of the density of the crucible (*e.g.* porcelain crucibles) to compensate for changes in pressure, density and humidity. For general use, it is convenient to scratch a mark on the inner wall of the crucible to indicate a volume of 10 ml. Solutions containing 0·1 to 0·5 mg. of nicotine were thus analysed with an average accuracy of ± 0·002 mg. It is necessary to make a correction (0·001 mg. per ml. of $N/20$ hydrochloric acid) for the solubility of nicotine silicotungstate. Precipitations have also been made in concentrations of acid up to $N/10$, with appropriate corrections for solubility. It is advisable to modify the acid concentration according to experimental conditions.

E. B. D.

Colorimetry with a Photo-electric Cell. P. Krumholz. (*Mikrochem.*, **1936, 20**, 227–235.)—Micro-colorimetric measurements are rendered much more accurate by the use of a photo-electric cell. Cells to hold small volumes of the coloured liquid are T-shaped, so that for the observation of a layer 20 mm. in thickness, about 1 ml. of the solution is required. By means of a lens-system the maximum amount of light from the source passes through the solution, and so to the photo-electric cell, the current of which is read on a micro-ammeter (measuring about 50 micro-amps. at 1700 ohm resistance). The sensitivity of the apparatus is regulated by varying the current through the lamp source of light. Schott's colour filters are used to filter the light for the different solutions, and for each measurement the filter that gives the maximum absorption is selected. Measurements of coloured solutions containing a few γ of the substance to be determined were made with errors of the order of 2 per cent. The apparatus is obtainable from P. Haack, Vienna. J. W. M.

Physical Methods, Apparatus, etc.

Application of Ultra-Violet Rays to Milling Products. H. Kühl. (*Mühlenlaboratorium*, 1936, **6**, 146–150.)—The beneficial effects which, it is alleged, irradiation by ultra-violet light of short wave-length produces on foodstuffs (*e.g.* milk) and water, suggest that the method may also be useful for bakery products (*cf.* Boner, *Mühle*, 1932, **69**, 646, 692; Owen, *Food Ind.*, 1932, **4**, 208). The author, however, thinks that this is unlikely, principally because bread, flour and grains of corn, etc., are solid materials, whereas the other products treated are mainly liquids, and therefore can be irradiated more efficiently. In connection with the well-known lethal effect of the radiations on certain growing organisms and insects (*e.g.* mites), the author confirms the fact that the surface colonies in a Petri-dish culture are destroyed more rapidly than those beneath. This may be due to ozonisation of the air by the radiations, or to the medium absorbing the radiation and so protecting the colonies below it. Chemical changes, beneficial and otherwise, may also be produced by the radiations, the browning of oak in sunny climates and changes in the chemical composition of the fatty matters of milk being instances of this; this effect is quite distinct from the activation of anti-rachitic principles also produced in the latter case, and it is the basis of

so-called "conditioning" processes for wheat. When seeds of wheat and vetch were exposed on a moist filter-paper to sunlight (behind window-glass) and to filtered ultra-violet light for 10 hours, germination was more rapid and stronger with the latter treatment; seeds which would not germinate in the sun could not be induced to do so by exposure to the ultra-violet light. Attempts were then made to destroy moulds or prevent mould-formation, natural moulds and specimens inoculated with *Penicillium glaucum* being used, and the seeds rolled slowly down an inclined plane so that the whole surface was exposed to the radiation for 2 to 5 minutes. Subsequent culture experiments on milk agar showed that the effect of the radiation had been negligible, and although better results were obtained using fine flour, they were still considerably inferior to those recorded for liquid food-products. It is concluded that the beneficial effects of the radiation are probably due to ozonisation, and that this can be produced more cheaply and conveniently by existing electrical methods. J. G.

Electrotor Dust and Smoke Meter. S. C. Blacktin. (*J. Ind. Hyg.*, 1936, **18**, 583–594.)—In selecting instruments for measuring the dust-contents of gases it is necessary to compromise between extreme accuracy so far as enumerating efficiency is concerned on the one hand, and speed, portability and general convenience on the other; as a rule, the latter considerations are the most important. The instrument described meets these requirements, but restricts as little as possible the range of concentration of dispersed articles that can be recorded and counted. It consists essentially of a pump (capacity 100 ml.), the plunger of which is moved by a hollow rod, whilst meshed vertically through the centre of the free face of the plunger is a length of archimedean screw which can thus revolve in and pass in or out of the hollow plunger-rod when the plunger is in motion. Attached to the archimedean screw is a celluloid or ebonite disc which revolves with the screw and thereby becomes electrified (by frictional rubbing) at the same time as the stream of the gas to be tested is set in motion by the action of the pump, the two effects being synchronous. As the incoming gas strikes the rotating electrified surface the dispersed particles are attracted to the disc, and as soon as they come into contact with it they are subjected to centrifugal force. The arrangement is such that the disc is being electrified whether the pump is being charged with the sample or discharged through the outlet valve provided, so that the electric field remains bound between the surfaces in sliding contact, including the portions of the surface of the disc where the record is not itself laid. The nature of the record is controlled by means of a stationary perforated nipple, the face of which is parallel to the disc. In this way the dirt in the air entering through the holes is deposited on the rotating disc in a regular manner in the form of concentric rings, the nature and width of which depend on the diameter of the holes, the nature of the sample and the volume analysed; the centrifugal force, moreover, aids the deposition of the particles according to size. The range of the instrument is increased by varying the number and positions of the ingress holes, and this is facilitated by means of a rotatable disc which slides over the upper face of the nipple in close contact with it, and is perforated with holes in the same relative positions as those in the nipple; various total record areas (*e.g.* from 0·12

to 24 sq.mm.) are therefore obtainable, by altering the angle through which the disc is turned. This device enables countable deposits to be obtained from heavy smoke or dust dispersions from 15 to 1,500,000 particles per ml., one stroke of the pump (occupying about 2 seconds) being adequate in every instance. The simultaneous use of several graded record areas on the same disc also enables rough comparisons of different samples to be made. Transparent or opaque discs are used according to the nature of the smoke, and these may be cleaned and re-used, or else trimmed and mounted and preserved on microscope slides 1 inch in width. Counting is carried out under the microscope on the most suitably-spaced deposit, and provision is made for deposition-areas up to 2 sq.mm., per ml. of gas analysed. J. G.

Obtaining from Mine Air Dust Particles for Physical, Chemical and Petrological Examination. H. H. Watson. (*J. Chem. Met. Mining Soc., S. Africa*, **1936, 37**, 166–188.)—In order to define completely an air-borne dust it is necessary to state the number and mass of the particles per unit volume, and their size, distribution, and chemical and mineralogical nature. It is generally agreed that the majority of particles found in the lungs are less than 5μ in diameter, and that few exceed 10μ. Dusts common to the mining industries should be evaluated by the use of a microscope having a magnification of 1500 (with a 2-mm. oil-immersion objective, and an eyepiece of magnification between $\times 15$ and $\times 20$). The impinger, konimeter, Owens' jet-dust counter and sugar-tube methods of sampling are critically surveyed, and it is concluded that all of them are open to objection, often serious, which makes them unsuitable for the purpose (*cf.* Green and Watson, *Med. Res. Counc., Special Rept. No.* 199, 1935; *J. Ind. Hyg.*, 1934, **16**, 29). A new method involving the use of a thermal precipitator and a salicylic acid filter (after Briscoe) is therefore described in detail. The former depends on the fact that if a hot body (*e.g.* an electrically-heated wire) is placed in an illuminated chamber containing a dust or smoke, a well-defined dust-free wedge-shaped space surrounding the hot body will become visible. Any particles of dust present follow the convection-curves set up by the body without penetrating the space, the thickness of which depends on the difference in temperature between the hot body and the surrounding air. In this way dust in air which is drawn slowly towards the wire (by means of a water aspirator) can be deposited on cover-glasses (size No. 1) inserted at the edges of the dust-free space, linear deposits of particles running parallel to the wire being obtained. The efficiency is 100 per cent. for particles up to at least 20μ in diameter, and for needle-shaped crystals (*e.g.* of asbestos) up to at least 50μ in length. The sampling-rate is 6·5 ml. per minute, and sampling may be continued for 30 minutes if necessary. The apparatus, which is portable, consists of two self-contained parts, each of which weighs 10 lbs. Provision is also made for incinerating the samples (*e.g.* to remove tarry matter) in a spirit lamp at about 450° C. for 15 minutes, and the deposits may be mounted on microscope slides for record purposes; it is also necessary to extract some mine-dusts with hot 50 per cent. hydrochloric acid for 15 minutes. The cover-glasses should be boiled with dilute hydrochloric and washed well before use. The size-distribution of the particles is determined

microscopically by means of a calibrated graticule, and it is most convenient to group the particles as follows:—Up to 0·2μ; 0·2 to 0·4μ; 0·4 to 0·8μ, etc.; 4 to 5μ; and over 5μ. Frequency curves may then be plotted. The object of the salicylic acid filter is to provide a reliable and convenient method of collecting 50 mg. of dust from 50 cb.m. of air. Such filters have a low resistance to air-flow, and they filter efficiently without clogging, while the dust may be removed without alteration by dissolving the salicylic acid in alcohol and centrifuging. For mine-dusts the A.R. acid should be ground, and 1·2 g. placed in the form of a pad in a shallow cell made from a fibre ring (thickness 0·05 inch, external diameter 5·3 cm., internal diameter 4·3 cm.) and a sheet of Whatman No. 40 filter-paper or a stainless-steel gauze (120-mesh). The paper or gauze is supported on a 20-mesh gauze, and the whole cell is held in an ebonite filter-holder and secured with a screw clamp. Before and after the test the top of the cell is covered with a sheet of cellophane (less than 0·001 inch thick), held in position by a rubber band. Three such cells are used in parallel, the sampling-rate (about 120 litres per minute) being measured by means of an ordinary household dry-gas meter (Smith high-capacity type) inserted between the compressed air ejector used to produce the suction, and the cell. The improved ejector described produces an under-pressure of 17 cm. of mercury with a maximum ejecting-capacity of about 600 litres per minute, air at a pressure of 60 lbs. per sq. inch being used. Full practical details are provided.

J. G.

Reviews

THE EXTRA PHARMACOPOEIA. (MARTINDALE.) Vol. I. Twenty-first Edition. Pp. 1072, Index pp. 109. Published by The Pharmaceutical Press, London. 1936. Price 27s. 6d.

The publication, in fifty-four years, of twenty-one editions of a work which has to be kept up-to-date, must be a record for anything of a scientific or technical character. The Martindales, father and son, gave between them, for fifty years, the personal attention and unique experience which yielded edition after edition of a book that became indispensable to the medical profession and to pharmacy; after their deaths, the work of revision had outgrown the abilities of one man, and so the Pharmaceutical Society took over the preparation of fresh editions, and, thanks to a Revision Committee and a competent editor, a new and comprehensive volume has just been issued. This Committee is comprised entirely of pharmacists, and the absence from it of any qualified medical practitioner does not appear to have caused any deficiency in the information on what, for want of a better term, may be called medical technique. It is a testimony to the fact that pharmacy is not only the hand-maid of medicine, but is willing and able to devise and give the needful *materia medica* in suitable forms for the use of physicians and surgeons.

This new edition differs slightly in size and arrangement from its predecessors, but the most noticeable and useful feature is its comprehensive index, which contains some thousands of references, including a great number to the other volume of "Martindale" (1935).

The attention of everyone will be struck by the tremendous number of names

of proprietary preparations used by the medical profession, and on consulting the pages their composition will be found, in most cases, in the actual words of the manufacturers. These do not consist of the so-called patent medicines, but of the "ethical" combinations whose properties are not for general broadcasting to the public, but are only ordered by the physician; with the continued increase of such preparations it seems imperative that every medical practitioner should possess this new "Martindale," and if the pharmacist is to be prepared to deal with modern prescribing, he, too, cannot afford to be without it.

The general arrangement of some of the subject matter is certainly more convenient than extending the number of headings, but it is only made possible by reference to the comprehensive index. For instance, it seems unusual to find such drugs as Bryony, Corydalis, and the alkaloid Bulbocapnine under the heading of Aconite, or Yerba Santa, Grindelia and Phytolacca classified with Ipecacuanha.

The sections dealing with Organic Arsenic Compounds and Barbitone (and the Barbiturates) are particularly informative, and mention all the numerous derivatives marketed under different fancy names, as well as their descriptions and properties.

Thyroid and its preparations have always received special attention in "Martindale." This has been continued and brought up-to-date, and the sections dealing with Oestrin, Insulin, Gland Products, Vaccines, Sera, Toxins and Antitoxins are now more complete than anything published elsewhere in such an accessible form.

The 1935 Poisons Rules are dealt with very fully, for now that medical practitioners, as well as dispensing pharmacists, have to conform to regulations, it is necessary for a doctor, or an analyst, to know the conditions under which poisons may be dispensed for patients, or under what restrictions they may be purchased or sold.

Useful summaries of the Therapeutic Substances Regulations, 1931, and of the Dangerous Drugs Consolidated Regulations, 1928, are presented in such a way as to make them easily understood—by no means an easy task. One of the most useful sections for reference is a comprehensive Therapeutic Index of Diseases.

In its modified form the book remains the "Martindale" to which we have become accustomed during so many years. The type is excellent, the proof-reading must have been truly rigorous and effective, and the resulting book will become a tribute to the Revision Committee and editor, for it has continued all that was good in former editions and added to it a vast amount of entirely new information of particular value to pharmacists, analysts, and physicians. C. E. SAGE

"ANALYTICAL CHEMISTRY" BASED ON THE TEXT OF F. P. TREADWELL. Translated, enlarged and revised by WILLIAM T. HALL. Volume II, QUANTITATIVE ANALYSIS. Eighth Edition. Pp. 858. New York: John Wiley & Sons; London: Chapman & Hall. 1936. Price 30s.

"Treadwell and Hall" has become one of the chief analytical classics in the English language, and, as such, a new edition is, perhaps, to be judged by not quite the same standards as, say, a first edition of a new book. Originally written, apparently, as a text-book for students, it has acquired a probably unintentional

reputation as a kind of inorganic "bible" to which one could turn in moments of difficulty. Whether these rôles are compatible is questionable; it is very obvious that what would be very excellent training for a student, combining diverse analytical operations in a number of separations drawn from widely different fields of inorganic chemistry, might easily be sheer exasperation and waste of time for a harassed analyst striving to get accurate results with the least possible expenditure of time and trouble for himself. As a laboratory manual for the practising analyst it has much to recommend it, much also that one would like to see altered. A notable weakness is that, amongst the multitude of methods given, there is an almost entire lack of critical data for assessing their relative merits; occasionally a process is said to give "accurate" results, though what degree of accuracy is never stated. Good, bad or indifferent, they stand shoulder to shoulder, and means of discrimination are not provided. A good example of this point occurs in the directions for standardising thiosulphate (p. 599); the first method given is with copper wire and is nothing more nor less than the ordinary iodimetric copper titration. Now it has been known for a long time that this reaction is not quite stoichiometric, and that the standardisation of thiosulphate in this way, though excellent for copper titrations, is slightly inaccurate for other purposes (*cf.* Foote and Vance, *J. Amer. Chem. Soc.*, 1935, **57**, 845). The second method given is with iodine, and here the meticulous "Treadwell" reasserts itself, and we are told not only to sublime but to resublime the iodine, and, furthermore, to cool it in a desiccator, the cover of which must not be greased and which must contain calcium chloride and not sulphuric acid. Pride of place being given to the copper method, the unwary chemist might well assume that this method, which has also the great merit of saving him a lot of time and trouble, is the one to adopt. If only a series of results obtained by every process could be given, the value of this undoubtedly valuable book would be increased enormously, and, in view of the number of students who must be constantly working through it, these results ought not to be difficult to obtain. There are many excellent processes, excellently described—in fact, clearness of description is a strong point throughout; on the other hand, there are some separations (chiefly relating to the analysis of technical products) which are distinctly crude, and one wonders why they have been included, as they seem to be rather off the beaten track for students and to be valueless for practising analysts. Even for students it seems a doubtful, though by no means uncommon, policy to force them through an impracticable scheme of analysis merely for the sake of the chemical facts they may pick up by the way.

The arrangement of the book strikes an analyst as extremely peculiar, but is probably due to the fact that its *raison d'être* is essentially teaching; it is hard to see, for instance, why a detailed description of the analysis of white lead (with one line about the determination of carbonate) should occur (pp. 347–8) in the middle of a section dealing with carbon dioxide; or why the spiritual home of a number of separations, *e.g.* iron, aluminium and phosphoric acid (p. 117) should be under the heading "Uranium." The preface states that "so many changes were made in the text that it was found best to reset the whole book"; this being the case, it is a great pity that much that is obsolete on the one hand, or of a rough "works analysis" type on the other, was not discarded. This especially applies to the

section on gas analysis, in which the latest reference is dated 1918, and only 12 out of 70 are subsequent to 1910, the table of heats of combustion being taken from Thomsen (1882), ignoring the classical work of Berthelot (1897).

Most of the metals are adequately treated, whether or no one agrees with all the methods given, but osmium is omitted altogether, and the section on cobalt is most disappointing. Considering the extensive analytical literature of cobalt, it seems to demand more than the two pages, or rather less, that are allotted to it; especially in view of the twenty pages given to the gravimetric determination of carbon dioxide and the fact that three different variants of the Gutzeit process are described, though the hypophosphorous acid precipitation of arsenic is not mentioned. On the other hand, it is refreshing to see so much space given to Dr. Schoeller's work on tantalum, etc.

With its various faults, however, "Treadwell" remains an outstanding text-book, and one which has gained considerably in passing into this new edition. Its value lies not merely in its description of processes—though most of these are sound and some very recent—but also scattered through its pages there are frequent comments whose broad analytical sanity is as praiseworthy as it is rare in such books. Specially noteworthy is the discussion on the separation of arsenic, antimony and tin from mercury, lead, copper, cadmium and bismuth (p. 228), and that on the precipitation of barium sulphate (pp. 411–414); there are excellent sections, too, on such subjects as membrane fillers, oxidation-reduction potential, adsorption indicators, etc.; occasionally, also, there are warnings which are too often overlooked, as, for example, that against igniting ferric hydroxide which has been washed with ammonium chloride solution (p. 99), and that against trying to reduce ferric salts completely with sulphur dioxide without first neutralising.

An analysis of the references (other than Gas Analysis) gives perhaps a clue to some of the elements of weakness in the book. Of the 593 references, there are 505 either German or American; of the 48 British references which come next, no fewer than 12 are to *The Chemical News*, mostly of a very early date, and 9 to the *Journal of the Chemical Society*; Dr. Schoeller's tantalum work accounts for another 13, leaving only 14 to cover the remainder.

The index, where tested, seems to leave a good deal to be desired; for instance, some references occur only in the author- and not in the subject-index; rhodium and ruthenium are not mentioned, and iridium only in connection with apparatus, though processes are given for their separation. Printing and production are of a high order, and very few misprints were noticed.

The book has an undeniable charm of writing, and one cannot but feel grateful for the provision, in the analysis of commercial hydrogen peroxide (p. 570), for the case (said to occur "frequently") where it contains no hydrogen peroxide at all. The new type of binding ("flexiback") appears to be very efficient in preserving the back of the book. B. S. EVANS

SCIENTIFIC AIDS FOR THE STUDY OF MANUSCRIPTS. By R. B. HASELDEN. Pp. x + 108. The Bibliographical Society, London. 1935.

This is a book that ought to be in the hands of every specialist who has anything to do with documents, for valuable manuscripts in many libraries and museums

have been severely injured, sometimes practically destroyed, owing to a lack of the knowledge contained in this work. Unfortunately, it is not designed for general circulation and sale, but it is to be hoped that an edition for this purpose will be issued. Every important library should at least know of the existence of the book.

Few, if any, writers are better supplied with material for the study of documents than Mr. Haselden, who, as Curator of Manuscripts in the Henry E. Huntington Library, California, has access to over a million manuscripts of all kinds and in all conditions. He discusses the subject of documents in a thoroughly scientific manner with accuracy, thoroughness and moderation, and avoids the unnecessary use of technical terms.

The book is beautifully printed by the Oxford University Press. It has a very complete index and is illustrated by sixteen interesting collotypes of the highest quality. As was to be expected in a work sponsored by the London Bibliographical Society, the extensive bibliographies at the end of each chapter are an outstanding and valuable feature, including foreign books and articles, and constituting probably the most complete collection of references relating to documents.

The introductory chapter discusses the procedure suggested for the general examination of a document, with six and a half pages of bibliography relating to the general subject. The second chapter treats of the care and handling of manuscripts, followed by another complete special bibliography. Chapter III is a discussion of light and colour as related to the subject, and Chapter IV treats of "Illuminants" and "Light Filters." In Chapter V the subject of microscopes and magnifiers is discussed, with special application to the subject of manuscripts. Chapter VI gives an account of the ultra-violet lamp and fluorescence, which is of increasing importance in investigating certain document problems, Chapter VII deals with photography, and Chapter VIII with measuring instruments and handwriting. The final chapter discusses examples of interesting and important manuscript problems, showing the great variety of problems that come before the examiner of documents.

Throughout this valuable work the many special instruments that are useful in the investigation of documents are described and discussed. Again and again the author lays stress upon the point that the mind of the observer is of greater importance than the instruments or process employed. "An examination of a document through the microscope," he remarks, "is useless unless the observer can correctly interpret the image of the object as seen when magnified." It is made clear that every scientific investigation is a process of reasoning and that one sees, not only with the eyes, but with the brain. ALBERT S. OSBORN

FIFTY YEARS OF FIELD EXPERIMENTS AT THE WOBURN EXPERIMENTAL STATION. By Sir E. JOHN RUSSELL and J. A. VOELCKER. Pp. 392. London: Longmans, Green & Co., Ltd. 1936. Price 21s. nett.

The Duke of Bedford and the Royal Agricultural Society in 1876 founded the Woburn Experimental Station as a means to carry out investigations that were not receiving attention elsewhere. The book is a review of the results of the work

and achievements of the Station, and it has recently been published as a Rothamsted monograph.

A few years ago a somewhat similar treatise was published which gave an account of the work and researches carried out at Rothamsted Experimental Station, but, alas, Gilbert and Lawes, who had directed the Station for more than fifty years, had both passed away. In the case of Woburn Station, though sixty years have passed since its foundation, this Jubilee book has been published during the lifetime of one who has been closely identified with the work of the Station throughout the period, and who has conducted the Station experiments for a period of over forty years, Dr. J. A. Voelcker. His many friends will rejoice to know that an account of what might be regarded as Dr. Voelcker's chief life work has been published while he is still an active worker in the cause of agriculture.

After an introduction dealing with the history of the Station, some fifty pages are devoted to the residual manurial values of cake fed to animals and with the continuous growth of cereals on the same land. Comment is unnecessary with regard to these first chapters, because their importance and significance are realised by everyone who has been interested in agriculture during recent years. Then green manuring with its attendant curious crop yields is followed by many short articles on different experimental enquiries.

Any doubt as to the justification for the existence of this Station should be dispelled by a glance at the headings of the various enquiries undertaken. Experiments embrace the feeding of stock and the cropping and manuring of soils, and are of so practical a value that few farmers can justly afford to neglect the knowledge gained by them. For instance, the use of condimental foods as a supplementary food for bullocks was investigated and found to be unnecessary and of no advantage; still the sale of condiments for this purpose is often pushed and at a price ranging up to £60 per ton.

The second part of the work, consisting of about one hundred pages, is devoted to a general statistical examination of the Station results. Here monthly averages of rainfall, or of sunshine hours, or perhaps of crop yields over periods, are depicted by means of curves or columns, which nowadays are so essentially a part of the equipment of the statistician.

Few, indeed, would attempt to assess the value of the Woburn Experimental Station's results to agriculture and, therefore, the chapter consisting of comments on the bearing of many of these results on agriculture forms one of the most interesting.

On a very early page is depicted the pot culture houses of the Station, but, strangely, no mention is made of the results obtained there. The pot culture work at Woburn was originally started to carry out investigations enjoined in the Hills Bequest of £10,000 to the Royal Agricultural Society. This embodied an enquiry into the possible part played in vegetation by mineral elements other than those of which the action and influence were ordinarily known. Dr. Voelcker experimented with a large number of such elements over a period of many years, and a very considerable number of reports have been published from time to time in the Journal of the Royal Agricultural Society. It seems at least unfortunate that some summary of this long and tedious, though interesting, work has not been

included in the volume under review. Hope may, however, be expressed that Dr. Voelcker will publish later a comprehensive account of this important feature of his work at Woburn.

The frontispiece is an excellent portrait of Dr. J. A. Voelcker, who has been in charge of the Woburn experiments since 1884. He and his collaborators are to be congratulated on this monograph, which will form a reminder of the Duke of Bedford and the Royal Agricultural Society, founders of the Station, and a permanent remembrance of Dr. Voelcker and his co-workers.

F. W. F. ARNAUD

AN INTRODUCTION TO COMPARATIVE BIOCHEMISTRY. By E. BALDWIN, B.A., Ph.D. Pp. xviii + 112. Cambridge University Press. 1937. Price 5s.

This fascinating book reached the reviewer with a message—a query, rather—from the Editor of THE ANALYST, whether it was yet another of those volumes "without which no biochemist is replete?" To this apparently simple question there is no simple answer, for one has in mind the *mot* of that anonymous French wit, to whom is attributed the request "Give me life's luxuries, and I will dispense with the necessities."

Dr. Baldwin opens up fascinating vistas down which the biochemist and the biologist walk hand in hand, reconstructing from analyses of blood and urine the morphology, physiology and environment of organisms known to us only as fossil remains. The concepts of uricotelism and ureotelism may be new to most analysts, but no one who reads Dr. Baldwin's 102 pages—all too few—is likely to overlook their importance. This particular aspect of comparative biochemistry is linked up with more general observations about the tonicity of blood and other body fluids and their evolutionary significance.

The answer to the Editor's question is, perhaps, after all, "Yes." This is not a text-book or, indeed, a utilitarian production of any kind. It is a luxury, but how much more welcome and stimulating than many necessities. On the chemist replete with ordinary biochemical text-books this speculative and philosophical essay will, maybe, act not unlike the glass of *fine* after a somewhat too overpowering meal.

A. L. BACHARACH

ELEMENTARY QUANTITATIVE ANALYSIS. By CARL J. ENGELDER, Ph.D. Second Edition, 1936. Pp. xiv + 270, with 12 illustrations. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price 13s. 6d. net.

Since the publication of the first edition, which was reviewed in THE ANALYST (1930, **55**, 356), the author has re-arranged the order of the subject-matter and has enlarged the text by the inclusion of some additional procedures, notably the analysis of hydrogen peroxide and pyrolusite and direct and indirect determinations of available chlorine in bleaching powder. A note on the use of ceric sulphate is also included.

The general excellence of the first edition is maintained, and, on the whole, the subject-matter calls for little comment. A few minor typographical errors may be pointed out. On pages 98 and 202 there are misprints for sodium and for

ferric hydroxide; on p. 20 "may be expect to lie" needs correction; and lastly, a curious phrase, "it is quite impossible and entirely too inaccurate," occurs on p. 31.

The book, as the name indicates, is intended for the use of elementary students commencing quantitative work in inorganic analysis. The manner in which the subject-matter is displayed and also the attractive and strong binding are worthy of praise.

H. R. NANJI

Publications Received

THE METABOLISM OF LIVING TISSUES. By ERIC HOLMES. With a Foreword by Sir F. GOWLAND HOPKINS. Pp. xi + 235. Cambridge: The University Press. Price 7s. 6d. net.

ENZYME CHEMISTRY. By H. TAUBER. Pp. xii + 243. London: Chapman & Hall. 1937. Price 15s. net.

SOAP: ITS COMPOSITION, MANUFACTURE AND PROPERTIES. Fourth Edition. By W. H. SIMMONS. Pp. xi + 140. London: Sir Isaac Pitman & Sons, Ltd. 1936. Price 3s. net.

LECTURE EXPERIMENTS IN CHEMISTRY. By G. FOWLES. Pp. xv + 564. London: G. Bell & Sons, Ltd. 1937. Price 16s. net.

A SCHOOL PHYSICS. By S. R. HUMBY and F. W. GODDARD. Pp. viii + 233. London: Longmans, Green & Co. 1937. Price 3s.

BRITISH CHEMICALS AND THEIR MANUFACTURERS. The Official Directory of the Association of British Chemical Manufacturers. 1937.

PRACTICAL ORGANIC CHEMISTRY. By F. C. MANN and B. C. SAUNDERS. Pp. xi + 403. London: Longmans, Green & Co. 1936. Price 8s. 6d. net.

APPLIED CHEMISTRY FOR ENGINEERS. By A. F. H. WARD. Pp. xi + 127. London: Longmans, Green & Co. 1936. Price 5s.

CHEMISCHE ANALYSEN MIT DEM POLAROGRAPHEN. By H. HOHN. Pp. vii + 102. Berlin: Julius Springer. 1937. Price RM.7.50.

CHEMICAL ARITHMETIC. By F. W. GODDARD. Pp. vii + 99. London: Longmans, Green & Co. 1937. Price 1s. 6d.