THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

An Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 2nd, the President, Dr. J. T. Dunn, being in the chair.

Certificates were read for the first time in favour of:—Lionel Stuart Davis, Arthur Smith, B.Sc., A.I.C., and Snow Blogburn Tallantyre, B.Sc., A.R.C.Sc., F.I.C.

Certificates were read for the second time in favour of:—Charles Ambrose Adams, B.Sc., F.I.C., Janet Warden Brown, Ph.D., A.I.C., and John Alexander Reddie, F.I.C.

The following were elected Members of the Society:—Ronald Gilbert Baskett, B.Sc., Hugh Charles Loudon Bloxam, F.I.C., Claud McClellan Bottomley, B.Sc., John Butler, B.Sc., F.I.C., Robert Ellison, A.M.C.T., George Noel Grinling, F.I.C., Albert Houlbrooke, M.Sc., A.I.C., Philip Henry Jones, F.I.C., Raymond Mallinder, Sydney Norman Herbert Stothart, B.Sc., Ph.D., A.I.C., and Hubert Threadgold, B.Sc., A.I.C.

The following papers were read and discussed:—"The Separation of Cadmium and Copper in Spelter and Zinc Ores by Internal Electrolysis," by Ella M. Collin, B.Sc., A.I.C.; "The Routine Detection of Nitrates in Milk," by A. F. Lerrigo, B.Sc., F.I.C.; and "A Method for the Determination of Titanium as Phosphate," by J. C. Ghosh, D.Sc.

NORTH OF ENGLAND SECTION.

A meeting of the Section was held in Manchester on April 12th. The Chairman (Mr. G. D. Elsdon) presided, and there were present the President (Dr. J. T. Dunn) and 19 other members.

An informal discussion took place on various problems of scientific and professional interest.

Obituary.

ARTHUR ANGELL.

THE death of Arthur Angell, our last original member, on February 3rd, severs a link with the far distant days when Charles Kingsley was at the height of his fame as a preacher and novelist, for the two men were friends and were closely associated in founding the Winchester Literary and Philosophical Society, now merged in the Hampshire Field Club. Angell's interests, indeed, were those of the naturalist rather than of the chemist, although chemistry became his profession.

He was the son of Mr. Arthur Angell of Winchester, and was born in 1844 at Basingstoke. He received his education at a private school at Holloway, London, and at the Queens' Grammar School, Basingstoke, and he entered upon his career as a chemist by becoming first a pupil of and then an assistant to Dr. Hassall, Public Analyst for Newport, Isle of Wight. Here Angell had, as his fellow assistant, Otto Hehner, and they worked together on the chemistry of butter fat, and ultimately devised the method of analysis which still bears Hehner's name. The results of this investigation were embodied in a book published in 1874, under the title of "Butter, its Analysis and Adulterations."

In the same year Angell started in practice for himself as an analytical chemist in Southampton, and soon after was appointed Public Analyst for the county of Southampton. Other appointments followed; in 1878 he became Public Analyst for the Borough of Guildford; in 1879 for the Borough of Newport, Isle of Wight; and in 1884 for the City of Winchester. Several of these appointments he still held at the time of his death.

He was one of the earliest Fellows of the Institute of Chemistry, being elected in 1878. Although an original member of the Society of Public Analysts, he never took a very active part in its proceedings, though in the early years he contributed short notes on the analysis of the water of private wells in Southampton (ANALYST, 1881, **6**, 65), and on the analysis of milk (ANALYST, 1884, **9**, 48). He was an expert microscopist and, like many of the early Public Analysts, was more interested in the microscopical than in the chemical side of his work. As early as 1876 he published a book on *The Microscopical Structure of Certain Fruits and Roots to be met with in the Jams and Preserves of Commerce*, which was reviewed in the first volume of THE ANALYST (p. 73); and later he published a pamphlet on the microscopical examination of water deposits. He was particularly interested in the biological aspect of this subject, and in 1882 he read a paper before the British Association on the cause of the discoloration of Southampton water.

Apart from the routine work of his practice, Angell took his share in the social activities of Southampton, and was at one time greatly appreciated as a popular lecturer on scientific subjects. In his youth he had been a prominent athlete, and in 1866 won the silver medal for general proficiency given by the National

Olympian Association for Promoting Physical Education; in his later years he was librarian to the Royal Southampton Yacht Club, of which in 1898 he was made an honorary life member.

Angell left a widow and a family of five, to whom the Council has conveyed the sympathy of the Society in their loss.

EDITOR.

The Separation of Metals by "Internal Electrolysis."

BY HENRY J. S. SAND, D.Sc., Ph.D., F.I.C.

(*Read at the Meeting, February* 5, 1930.)

THE analytical method to be described, for which I suggest the name "internal electrolysis," should, I believe, prove useful, more particularly in cases in which it is desired to separate a small quantity of one metal from much larger amounts of another, more electropositive (baser) than itself. It is, however, by no means limited in its application to any particular ratio of the two constituents to be separated. Particulars are given in other papers by Miss E. M. Collin of the determination of small amounts of bismuth and copper in lead bullion, and of cadmium and copper in spelter. A method similar in principle has been described by Hollard for the separation of zinc from nickel (*Bull. Soc. Chim.*, 1903, **29**, 116, and "Analyse par Electrolyse," Paris, 1906, p. 23). The metal to be determined is deposited on a platinum cathode, the essential feature being that no electric current is introduced from outside, but instead, an anode of the baser metal is employed, which is placed in contact with a solution of one of its salts in a compartment separated by a parchment membrane from the solution to be examined. The present apparatus is designed so that efficient circulation of the catholyte is produced by mechanical stirring, and if any of the metal to be determined has found its way into the anode compartment by diffusion or otherwise, the whole of the anolyte may be washed into the cathode compartment.

The process differs from that of Hollard in the following particulars:

(1) Hollard places his zinc anode in a solution, not of a zinc salt, but of one of magnesium. During an analysis zinc dissolves, and a state of affairs thus establishes itself similar to that contemplated in the method at present under description. There appears, however, to be some risk, that when a solution containing a high concentration of zinc and a low one of nickel is analysed, some zinc may at first be deposited with the nickel, owing to the high electromotive force available. This high electromotive force is obviously avoided by placing the anode in a suitable solution of one of its own salts.

(2) Hollard's arrangement does not allow stirring of the catholyte, and must hence be classed with the "slow" methods of electrolytic analysis; whereas it will be shown that the method to be described allows small quantities of bismuth and cadmium to be quantitatively deposited in about a quarter of an hour.

(3) Hollard's apparatus does not permit the anolyte to be washed into the cathode compartment. This, in conjunction with the greater length of time required for a determination, somewhat limits its applicability. Thus Hollard

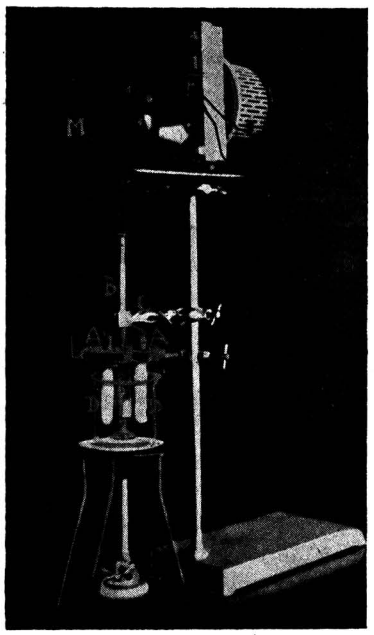

Fig. 1.

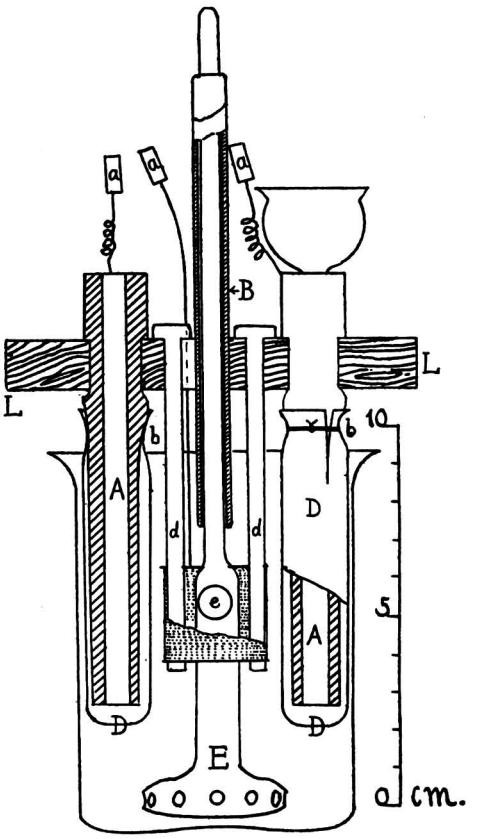

Fig. 2.

states that his method cannot be employed for the determination of copper—a limitation which does not apply to the method here described.

Figure 1 shows the general arrangement of the apparatus, while Figures 2 and 3 explain details. The two anodes, the cathode and the stirrer, are fitted to the circular wooden lid *L*, shown in detail in Figure 3, which rests on a ring held by a retort stand, as shown in Figure 1. A sector is cut away from the lid and a corresponding piece from the ring, in order to allow the wire, which serves as the connection with, and suspension of the cathode, to be readily placed in position. The

lid may be divided into halves, held together by dowels and by hooks, as shown, in order to allow the anodes to be fitted more readily into position.

The anodes are hollow, and those of the form shown were cast in lead. Leading-in wires were attached which were soldered to small plates of platinum foil, *a*. The leading-in wire to the cathode carries a similar plate, *a*, and connection between the electrodes was made by clamping the plates against each other and against the guide tube, *B*, for the stirrer by means of the clamp, *C* (Fig. 1). Alternatively, the connecting wires to the anodes may be permanently soldered to the clamp, the connection to the cathode being made with the jaw, which is bared of cork for this purpose. The anodes must be shaped so that the parchment diaphragms, *D*, may be tied securely to them by thread. The latter consist of parchment thimbles, of 16 mm. diameter, which are cut to a length of about 8 cm. Slots are cut into these lengthwise at the top to a distance of about 2 cm. This allows them to be

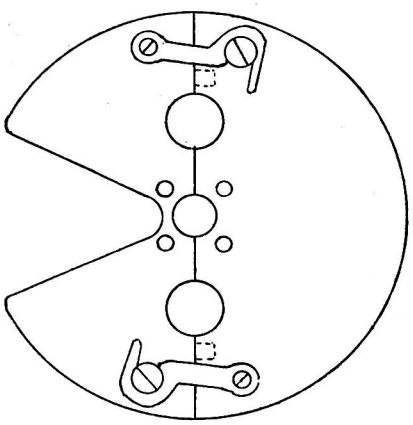

Fig. 3.

pulled over the recessed portions of the anodes at *b*, and tied securely to them. It also allows liquid from the anode chamber to be forced into the cathode chamber by running fresh electrolyte from underneath it. The anode chambers are filled by means of funnels introduced into the hollow anodes, as shown in Fig. 2. The same thimbles may be used an almost indefinite number of times, according to the nature of the electrolyte. Instead of cast anodes, it has frequently been found more convenient to employ anodes built up by winding the metal in strip form around glass tubes of about 1 cm. external diameter.

The cathode, *D*, is a platinum gauze cylinder of 2·5 cm. diameter and height, the leading-in wire is of 1 mm. thickness and about 12 cm. length. The cathode is held in position by four glass rods, *d*, over which it is slipped from below, and it is suspended by its leading-in wire. The glass rods are held by the lid, being passed through four holes provided for the purpose. They are prevented from falling through by buttons fused on to the top.

The stirrer, *E*, is of the centrifugal type. At the bottom it consists of a lenticular bulb of 3·7 cm. diameter, fitted with twelve holes. The lower portion of the stem is hollow to a height of about 6 cm. from the bottom of the stirrer; it is of about 1·1 cm. external diameter and has two holes, *e*, opposite each other at the top, of about 8 mm. bore. These holes should be opposite the centre or near the top of the cathode, so that when the stirrer is revolved, vigorous suction takes place here, the liquid being ejected at the bottom. The stirrer revolves inside the glass tube, *B*, already referred to, which is fitted to the wooden lid. The motor, *M*, with its back resistance, is visible in Figure 1. Its method of attachment to the wooden boards, *F*, which are tightly clamped to the top of the rod, will require no further explanation. It is protected from fumes by a uralite slab, visible in the figure, which rests on a ring. Connection with the rod of the stirrer is made by means of a piece of thick-walled rubber tubing. The number of revolutions is adjusted to the maximum which appears consonant with safety.

METHOD OF WORKING.—Before assembling the apparatus for use, the cathode, stirrer and tripod are removed. The cathode is weighed, placed in position, and connected with the anodes by means of the clamp, *C*. The stirrer is then inserted, and the beaker, of about 350 c.c. capacity, which usually contains about 200 or 250 c.c. of liquid, placed in position, the tripod being pushed beneath it. For disconnecting, these operations are successively reversed, the electrode is washed, and then dipped successively into jars of alcohol and ether, dried over a burner, and weighed after being allowed to assume the temperature of the balance.

SIR JOHN CASS TECHNICAL INSTITUTE, E.C.3

The Rapid Determination of Bismuth and Copper in Lead Bullion by Internal Electrolysis.

BY ELLA M. COLLIN, B.Sc., A.I.C.

(*Read at the Meeting, February* 5, 1930.)

BISMUTH occurs frequently in small quantities in lead ores, lead bullion and other commercial lead products, and its accurate determination is of great importance. For small amounts of bismuth the electrolytic separation from lead by grading the potential with the aid of an auxiliary electrode is not satisfactory, and the method here described was devised for the determination of amounts of bismuth less than 0·01 grm. in the presence of up to 10 grms. of lead, since the percentage of bismuth present in a lead product is usually less than 0·10 per cent.

The work was done with the internal electrolysis apparatus designed by Dr. Sand for this purpose and described by him in a separate paper. Preliminary

experiments were made with a cathode of platinum foil in the shape of an inverted T, the horizontal limb of which was bent to form a small vertical cylinder, but subsequently a gauze electrode was used, as it was found that the deposit was much more adherent and satisfactory.

THE SEPARATION OF BISMUTH FROM LEAD.—Ten grms. of pure lead were dissolved in 60 c.c. of 20 per cent. nitric acid, heated gently, and the excess of acid neutralised with ammonia; then 3 c.c. of concentrated nitric acid were added, the solution was diluted to 200 c.c., and 3 drops of a 50 per cent. solution of hydrazine hydrate (Kahlbaum) added to decompose any oxides of nitrogen present. In subsequent experiments hydroxylamine hydrochloride was used, as it is much cheaper and equally effective. A standard solution of bismuth in nitric acid was added in known amount, and the solution electrolysed in the apparatus as described elsewhere. Experiments at a temperature below 80° C. were unsatisfactory, as the deposit was spongy and non-adherent. When the electrolysis was done at a temperature of 85–90° C., the bismuth deposited was light grey in colour and very adherent. The anode compartments contained a 5 per cent. solution of lead nitrate, acidified with nitric acid. At the conclusion of each electrolysis the electrode, after washing with water, was dipped successively in alcohol and ether, and dried by holding it some distance over a Bunsen flame, care being taken not to ignite the ether. In all the experiments described in this paper, it was found unnecessary, owing to the low percentage of the metal to be determined, to wash out the anode compartment before the conclusion of the electrolysis.

TABLE I.

Bismuth added. Grm.	Bismuth found. Grm.	Time. Minutes.	
0·0050	0·0049	13	
0·0050	0·0047	11	
0·0040	0·0038	15	
0·0040	0·0037	15	(continued another 5 minutes; no increase in weight)
0·0050	0·0051	17	do. do.
0·0040	0·0042	17	

In addition to bismuth, the impurities present in lead bullion and likely to interfere in this method are copper, silver and antimony, and experiments were made to find means of eliminating the effects of these elements.

EXPERIMENTS IN TARTRATE SOLUTION.—Lead bullions containing much tin or antimony do not give a clear solution in nitric acid, and the precipitate may contain some of the bismuth present in the sample. A clear solution can, however, be obtained by the use of a mixture of nitric and tartaric acids for dissolving the sample, and it was found that the presence of tartaric acid in the electrolyte was in no way detrimental to the deposition of bismuth and copper. The solutions were prepared and the electrolysis carried out as described for the separation of

bismuth from lead in nitric acid solution, with the exception that 1 grm. of tartaric acid was added to the nitric acid used for dissolving the sample.

TABLE II.

Bismuth added. Grm.	Bismuth found. Grm.	Time. Minutes.
0·0050	0·0049	10
0·0050	0·0050	10
0·0050	0·0048	10
0·0050	0·0048	10
0·0015	0·0014	10
0·0035	0·0036	10
0·0025	0·0025	10
0·0050	0·0050	10

It was found necessary to keep the surface of the lead anodes scraped free from the deposit of lead tartrate which tended to form on them.

SILVER.—Most lead bullions contain silver, which would be deposited during the electrolysis and cause a loose deposit, but this metal can be removed satisfactorily by the addition of a small amount of hydrochloric acid, the deposition of bismuth being unaffected by the presence of small amounts of chlorides, and there being no deleterious action on the platinum cathode.

ANTIMONY.—A standard solution of antimony was prepared by dissolving metallic antimony (Kahlbaum) in a mixture of nitric and tartaric acids, and known amounts were added to a solution of lead prepared as described above and electrolysed. Erratic results were obtained, and only a small proportion of the antimony was deposited. The standard solution was found to contain some trivalent antimony, contrary to expectations from the method of its preparation. Investigations with a freshly-prepared solution of antimonious chloride showed that trivalent antimony was completely deposited.

TABLE III.

Antimony added (as $SbCl_3$). Grm.	Antimony found. Grm.
0·0132	0·0130
0·0132	0·0136
0·0132	0·0134
0·0132	0·0132

In each case the solution after electrolysis was tested and found to be free from antimony.

Experiments with antimonic chloride showed that pentavalent antimony was not deposited under the conditions of experiment.

It was not found possible to reduce pentavalent antimony to the trivalent condition in a solution which would be suitable for subsequent electrolysis, hydroxylamine, hydrazine, phosphite, hypophosphite and potassium iodide being tried

without success. As it was found impossible to reduce antimony with a view to its subsequent quantitative determination, experiments were made to find the most suitable oxidising agent for converting any trivalent antimony present into the pentavalent state. Potassium dichromate, and potassium chlorate were not satisfactory, but potassium permanganate gave good results, and, by the addition of a 2 per cent. solution of this reagent until it was no longer decolorised (the excess being removed by the subsequent addition of hydrazine or hydroxylamine), the antimony was converted completely into the pentavalent condition and its deposition inhibited. The tartaric acid present does not react with the permanganate, provided the solution be cold.

COPPER.—Copper is deposited under the same conditions as bismuth, and therefore in the electrolysis of a solution containing both these elements they will be deposited together. Experiments were made on the deposition of copper with this apparatus both alone and together with bismuth. The solution for electrolysis was prepared as described above in the separation of bismuth from lead, and the results are shown in Table IV.

TABLE IV.

Copper added. Grm.	Bismuth added. Grm.	Weight of metal deposited. Grm.
0·0006	Nil	0·0006
0·0062	Nil	0·0063
0·0063	0·0030	0·0094

The most rapid and satisfactory way of separating the combined deposit was found to be the usual method, employing ammonia and ammonium carbonate. The deposit is dissolved in a small amount of nitric acid (1: 1). The type of electrode used allows this operation to be carried out in a small beaker of about 50 c.c. capacity. The electrode is then carefully washed with water, the solution is neutralised with ammonia, and ammonium carbonate added in slight excess. The liquid is warmed gently to facilitate the settling of the precipitate and then filtered, the precipitate being washed with 2 per cent. ammonia. The filtrate is acidified with nitric acid with the addition of an excess of 2 c.c. of concentrated acid, the solution heated to about 80° C., and electrolysed in the same apparatus used for the first deposition, in a volume of about 200 c.c. The precipitate is dissolved in dilute nitric acid and electrolysed in the same way as the copper at a temperature of 85–90° C. As a rule it was not found necessary to make a double separation of the bismuth and copper, as the bismuth deposited after the first separation was found to be free from copper, but when the amount of copper present is more than about 0·03 grm. it is advisable to test the bismuth deposit to ensure that the separation is complete.

The following experiments were carried out by adding known amounts of bismuth and copper to a solution containing 10 grms. of lead as nitrate and 1 grm.

of tartaric acid, which was prepared and electrolysed as described above, and the combined deposit then separated. Each electrolysis was carried out for 10 minutes.

TABLE V.

	Amount added. Grm.	Amount found. Grm.
Bismuth	0·0040	0·0039
Copper	0·0071	0·0070
Bismuth	0·0050	0·0051
Copper	0·0030	0·0028
Bismuth	0·0040	0·0038
Copper	0·0050	0·0048
Bismuth	0·0035	0·0036
Copper	0·0025	0·0025
Bismuth	0·0030	0·0030
Copper	0·0025	0·0025
Bismuth	0·0030	0·0030
Copper	0·0025	0·0025
Bismuth	0·0035	0·0033
Copper	0·0030	0·0031

From the experiments described above it is shown that, under suitable conditions, the bismuth and copper present in a sample of lead bullion can be deposited together free from other elements and can then be separately determined.

METHOD FOR THE DETERMINATION OF BISMUTH AND COPPER IN LEAD BULLION. —Five grms. of the sample are dissolved in 50 c.c. of 20 per cent. nitric acid, with the addition of 1 grm. of tartaric acid. (If the bismuth content is known to be low, 10 grms. of the sample are taken and the amount of nitric acid increased proportionately.) Two c.c. of 2 per cent. hydrochloric acid are added, and the precipitate of silver chloride is allowed to coagulate at a gentle heat, and then filtered. off, together with any insoluble residue from the lead. The precipitate is washed well with hot water, and the filtrate is diluted to about 100 c.c. and cooled; then a 2 per cent. solution of potassium permanganate is added as long as it is decolorised, to convert any trivalent antimony present into the pentavalent condition. Five c.c. of a 5 per cent. solution of hydroxylamine hydrochloride are added, and the solution, after dilution to about 200 c.c. in volume, is electrolysed in the internal electrolysis apparatus at a temperature of 85–90° C. for 15 minutes. It was not found necessary to neutralise the solution and re-adjust the acidity prior to electrolysis as in the earlier experiments, since the excess acid remaining after the solution of the sample was sufficient. The combined deposit of bismuth and copper is treated as described above. It is not necessary to weigh the deposit before separation, except as an additional check if both the bismuth and copper are to be determined.

It was found, during the course of several experiments, that the deposition was complete in every case after 15 minutes, and that a further period of electrolysis gave no increase in weight of the deposit; but should the deposit contain

more than about 8 mgrms. of bismuth, it is advisable to replace the electrode after the removal of the deposit, to ensure complete deposition. Any additional metal deposited can be combined with the original deposit. A much larger amount of copper than of bismuth can be deposited in the stated time, and up to 0·05 grm. of this metal can be accurately determined, but the amount of bismuth present should not exceed 0·01 grm., as larger quantities do not adhere satisfactorily to the electrode.

RESULTS.—The experiments recorded in Table VI were made by starting from pure lead (5 or 10 grms. being taken), to which known amounts of bismuth and copper, and unknown amounts of antimony and silver, were added.

TABLE VI.

	Amount added. Grm.	Found. Grm.	
Bismuth	0·0050	0·0051	
Copper	0·0080	0·0081	
Bismuth	0·0030	0·0028	
Copper	0·0035	0·0036	
Bismuth	0·0030	0·0027	
Copper	0·0025	0·0023	
Bismuth	0·0035	0·0025	(Bi found in second
Copper	0·0030	0·0029	electrolyte)
Bismuth	0·0036	0·0034	
Copper	0·0025	Solution lost	
Bismuth	0·0037	0·0037	
Copper	0·0030	0·0027	
Bismuth	0·0037	0·0037	
Copper	0·0025	0·0023	

In Table VII are shown the results of analyses of samples of commercial lead bullions, by the electrolytic method described above and by Rowell's method (*J. Soc. Chem. Ind.*, 1908, **27**, 102).

TABLE VII.

Sample number.	Bismuth. Electrolytic. Per Cent.	Bismuth. Rowell's method. Per Cent.	
1.	0·104	0·115	
2.	0·064	0·069	
3.	0·060	0·069	
4.	0·042	0·044	(sample contained about
5.	0·060	0·068	2 per cent. of copper)
6.	0·068	0·066	
7.	0·068	0·068	
8.	0·068	0·068	
9.	0·026	0·028	(sample contained about 1 per cent.of copper)

The copper content of these samples was about 0·1 per cent., except Nos. 4 and 9. In the case of No. 4, a single separation of bismuth and copper was sufficient, but in the case of No. 9 a double separation was necessary, as the bismuth deposited electrolytically after the first precipitation was found to contain traces of copper.

SUMMARY.—A new electrolytic method for the separation of small quantities of bismuth and copper from large amounts of lead is described, in which the lead is made to displace the less basic metals from solution without any external E.M.F. The principle is applied to the analysis of lead bullion, other impurities being either precipitated or precautions taken to prevent their deposition.

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

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

The Precipitation of Small Amounts of Lead as Chromate, and their Accurate Colorimetric Determination.

BY B. JONES, B.Sc., A.I.C.

THE precipitation of lead as chromate has formed the basis for the determination of the metal in many substances, either directly, or after an initial separation as sulphate when the lead is present in fairly appreciable amounts, for the chromate appears to be the least soluble salt of lead under certain conditions. A widely-practised method for the removal of lead from solution is by the formation of its sulphate after heating with sulphuric acid until fumes appear, but, although this method is a very useful means of removing lead from other metals, yet, at its best, it leaves a little lead in solution, owing to the definite solubility of lead sulphate in dilute sulphuric acid; hence, the method is not sufficiently accurate for the separation of very small amounts of the metal, except under special conditions which include a long period of standing (Francis, Harvey and Buchan, ANALYST, 1929, **54**, 645).

Many papers have been published dealing with the determination of traces of lead in water, urine, oils, metals, minerals, etc., by methods in which the lead is separated as the sulphide, with or without the addition of a little copper, the precipitate being dissolved in acid, and the lead determined colorimetrically as the colloidal sulphide by the addition of cyanide and alkaline sulphide. It has been shown in several communications that this method is unsatisfactory, probably owing to differences in the tint of the standard solution and to the fact that more than 0·1 mgrm. of lead cannot be used for comparison without incipient precipitation of the sulphide producing a turbidity. There seems room, therefore, for a colorimetric method that will deal quantitatively with amounts of lead of

the order of 0·1 mgrm. and over. Evans (ANALYST, 1928, **53**, 626) separated small amounts of lead by deposition on copper, converted the lead into sulphate, which was dissolved in ammonium acetate and then converted into the chromate; the solution was boiled and allowed to stand overnight, and the lead determined by dissolving the precipitate in acid and matching the yellow colour with standard potassium dichromate. This method gives very good results, but it is difficult to detect amounts of lead less than 1 mgrm., as the colour is not sufficiently sensitive for these amounts; and to obtain quantitative results it is necessary to let the lead chromate precipitate settle overnight.

Kehoe, Edgar, Thamann and Saunders (*J. Amer. Med. Assoc.*, 1926, **87**, 2081) described a method for the determination of lead in urine in which the acid solution of lead was taken to dryness and the residue heated at 160° C. for 1½ hours; and then dissolved in water the solution was poured into an excess of *N*/100 potassium dichromate solution and shaken with asbestos for ten minutes, and the excess of dichromate determined colorimetrically.

Accurate results have not been obtained by this method, as when a solution containing small amounts of lead is heated, as described, the residue is not completely soluble in water, owing to the formation of a little basic salt of lead, and the addition of some mineral acid is necessary to ensure a clear solution; but, in the presence of a trace of acid, the method fails.

THE ACCURATE DETERMINATION OF LEAD IN THE PRESENCE OF MINERAL ACID.—After many experimental tests, quantitative precipitation of small amounts of lead as chromate was effected in the presence of hydrochloric acid as follows: The acid solution of lead is evaporated to dryness on a water-bath, 8 drops of dilute (1 : 1) hydrochloric acid are added, and then hot water. To the clear solution thus obtained, 10 c.c. of approximately *N*/10 potassium chromate solution are added, and the liquid made just alkaline with dilute ammonia, which is added, drop by drop, and the solution is then *just* re-acidified with dilute (1 : 1) acetic acid (about 3 drops are required), *i.e.* until the greenish colour just changes back to orange-yellow. The solution is now boiled for 10 minutes, after which the vessel is immersed in running water for 15 minutes. The lead chromate separates out as a well-crystallised precipitate; it is collected off on asbestos pulp, and washed well with 2 per cent. potassium nitrate solution until the filtrate is colourless.

It is then dissolved by the addition of 10 c.c. of nitric acid of sp. gr. 1·2 (from which the nitrous fumes have been driven out by boiling), the solution is passed through the filter two or three times into a 100 c.c. Nessler glass, and the pulp is washed with water until colourless, when the solution is made up to the 100 c.c. mark. The same amount of acid is put into another 100 c.c. Nessler glass, diluted to the mark, and 5 c.c. of a 0·1 per cent. solution of diphenylcarbazide in dilute acetic acid are added to each of the Nessler tubes. The strong permanganic colour of the solution under examination is matched by titrating the liquid in the other Nessler tube with a standard solution of potassium dichromate until the colours match. When the colour of the solution under examination is of a definite yellowish tint, *i.e.* when more than 1 mgrm. of lead is present, there is no need to

add the organic indicator, as quite accurate results are obtained by matching the yellow colour. An advantage of the method is that it is very sensitive, and yet it will deal also with amounts of lead of the order of a few mgrms.

The following amounts of a dilute solution of lead nitrate were taken and treated as described above. A fresh solution of lead was always taken, as it was noticed that dilute solutions apparently hydrolyse on standing.

Lead taken. Standard solution.	Grm.	Colorimetric reagent.	$K_2Cr_2O_7$ used. c.c.	Lead recovered. Grm.
1 c.c.	= 0·0001	5 c.c. of diphenylcarbazide	1·5 N/1000	0·0001
2 c.c.	= 0·0002	,, ,, ,,	3·0 ,,	0·00021
2·5 c.c.	= 0·00025	,, ,, ,,	3·5 ,,	0·00024
4·0 c.c.	= 0·0004	,, ,, ,,	0·6 N/100	0·00039
5.0 c.c.	= 0·0005	,, ,, ,,	0·8 ,,	0·00055
7·5 c.c.	= 0·00075	,, ,, ,,	1·1 ,,	0·00076
*10·0 c.c.	= 0·0010	chromate colour compared	1·6 ,,	0·0011
*20·0 c.c.	= 0·0020	,, ,, ,, ,,	2·9 ,,	0·0020
*30·0 c.c.	= 0·0030	,, ,, ,, ,,	4·4 ,,	0·0030

1 c.c. N/100 $K_2Cr_2O_7$ = 0·00069 grm. Pb.

* Large crystalline precipitates.

EFFECT OF AMMONIUM ACETATE ON THE PRECIPITATION OF LEAD AS CHROMATE.—It was noticed that the presence of an excess of ammonium acetate has a distinct solvent effect on lead chromate. The following amounts of lead were taken, ammonium acetate was added to some of them, and then an excess of potassium dichromate solution.

	Lead taken. Grm.	Amount of ammonium acetate added.	Remarks.
(*a*)	0·001	None	Precipitate of lead chromate formed at once.
(*b*)	0·001	5 drops	Precipitation was delayed.
(*c*)	0·001	20 c.c.	Precipitation was inhibited.

To (*a*), after formation of the precipitate, ammonium acetate solution was added, drop by drop, with the result that the precipitate dissolved completely and did not reappear, even on boiling. When (*c*) was boiled for 15 minutes, and allowed to stand overnight, a small very dense precipitate was obtained, which appeared to be in a different physical form from the precipitates obtained as described above. The effect of boiling, therefore, appears to involve the partial destruction of the acetate, and then re-precipitation of the lead chromate takes place, when quantitative results are obtained after standing overnight. The solvent effect of ammonium acetate does not appear to manifest itself so completely when large amounts of lead are precipitated as chromate, but with small amounts of lead the amount of ammonium acetate present in the lead solution must be kept well under control.

DEPT. OF METALLURGY,
UNIVERSITY COLLEGE, CARDIFF.

The Detection and Determination of Oxalic Acid and Oxalates in Stomach Contents

By G. D. ELSDON, B.Sc., F.I.C., and J. R. STUBBS, M.Sc., F.I.C.

(*Read at the Meeting of the North of England Section, February 15th*, 1930.)

From time to time we have had occasion to determine the amount of oxalic acid present in stomach contents, and have therefore examined the various methods suggested in the standard works on toxicology. There would appear to be five general procedures specified, which are:—

(1) Evaporation to dryness, and extraction with alcohol, as in the detection of alkaloids. (2) Precipitation with lead acetate solution, filtration, decomposition of the precipitate with hydrogen sulphide, filtration and precipitation of the filtrate with calcium chloride solution. (3) Digestion with hydrochloric acid, filtration and precipitation of oxalates in the filtrate with ammonia and calcium chloride. (4) Dialysis. (5) Extraction of oxalic acid by means of ether.

(1) By comparing the results obtained by various methods, it was early found that even repeated extraction with alcohol was unsatisfactory. Thus, in one experiment the alcoholic extract contained the equivalent of 0·122 grm. of oxalic acid, whilst the insoluble residue contained 0·272 grm. These results have been repeated on several occasions, and it would appear that the method is quite unsatisfactory.

(2) This method has given fairly satisfactory results, the chief difficulty being the slow rate of filtration after the first precipitation with lead acetate solution. As a rule, the precipitation with lead acetate must be repeated, after which the precipitate produced with calcium chloride is usually white, and, in most cases, sufficiently pure without further treatment. The process gives results which are apparently accurate, at least as judged by comparison with method (3) below. Two determinations in the same sample gave 1·14 per cent. and 1·13 per cent. of oxalic acid. The amount of manipulation involved is large, and the necessity for washing bulky precipitates renders the method open to some objection. It is apparently capable, however, of giving results of considerable accuracy.

(3) This method would appear to be, on the whole, the simplest and best. It may be carried out in the following manner:

A suitable quantity of the liquid, diluted with water if necessary, is whirled in a centrifuge for some minutes. The liquid is decanted as completely as possible, and the residue broken up with a glass rod, mixed with a quantity of water equal in bulk to the original volume of the liquid and again centrifuged, and the liquid decanted and mixed with the first decanted portion. The washing may be repeated, if necessary.

In general, the residue will be free from oxalates, but it should in all cases be treated with hydrochloric acid and tested for oxalates by the same method as the solution.

The combined solution and washings are mixed with 15 to 20 per cent. of concentrated hydrochloric acid and heated in the water bath for about two hours. After this treatment the liquid is filtered and the precipitate washed, it then being in such a condition that this can readily be done. The mixed filtrate and washings are made alkaline with ammonia, and then acid with acetic acid (0·880 ammonia and concentrated acetic acid should be used to keep down the bulk), and the oxalic acid precipitated with calcium chloride solution in the usual way. The precipitate is invariably coloured, and a second or even a third precipitation may be necessary. The precipitate is dried at 100° C., and weighed as calcium oxalate ($CaC_2O_4.H_2O$). The precipitate may be dissolved in hot dilute sulphuric acid and titrated with $N/10$ permanganate solution.

The amount of oxalic acid obtained from the titration should agree with that found by weighing; this affords a confirmation of the qualitative tests.

The effect of boiling oxalic acid with hydrochloric acid has been tried both with solutions containing 10 per cent. and 20 per cent. of the concentrated acid, and no diminution of the amount of oxalic acid has been observed.

(4) Dialysis has been suggested by several observers as a means of removing oxalates from admixture with stomach contents. This method has been tried, but with indifferent success. As a qualitative method, it has some advantages, but it is, in general, too slow for quantitative work, and the dialysed solution is by no means as free from interfering organic impurities as might be expected.

(5) Some text-books assert that oxalic acid may be extracted from organic solutions by means of ether, although Wynter Blyth denies that this is the case. The opinion of Wynter Blyth has been confirmed. A solution containing 0·455 grm. of oxalic acid was thoroughly extracted three times with ether, the ether allowed to evaporate spontaneously, and the residue weighed; six mgrms. had been extracted.

THE QUALITATIVE TESTS FOR OXALIC ACID.—An organic acid which reduces permanganate and which gives a precipitate with calcium chloride, insoluble in acetic acid, is not necessarily oxalic acid. It may, for example, be tartaric acid. Treadwell (*Analytical Chemistry*, Vol. I, 6th Ed., p. 388) states that calcium tartrate is soluble in acetic acid, and that this property distinguishes this salt from calcium oxalate. This, however, is not the case, calcium tartrate not being appreciably soluble in acetic acid. The properties are correctly given in Dr. C. A. Mitchell's translation of Fresenius, 17th Edition, page 500. When carried out in dilute solution containing acetic acid, the character of the precipitation is such that no error is likely to arise. Thus a solution containing the equivalent of 1·0 per cent. of oxalic acid acidified with acetic acid, gives an immediate precipitate in the cold, whilst a similar solution containing tartaric acid gives no precipitate until it is allowed to stand or the solution is shaken. A similar solution containing the equivalent of 0·01 per cent. of oxalic acid, gives a turbidity almost immediately, whilst a solution of tartaric acid of similar strength gives no turbidity on vigorous shaking.

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Notes.

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

DETERMINATION OF MINUTE AMOUNTS OF LEAD AND COPPER IN FOOD, BEVERAGES, ETC.

If the substance yields very little or no ash, it is advisable to add about 0·20 grm. of calcium hydroxide as a fixative, to prevent combination of traces of lead and copper with the platinum or silica of the vessel used for incineration.

Malt, Beverages, etc.—One hundred c.c. are evaporated to a syrupy consistence in a silica dish. A large Bunsen burner, made entirely of iron, is clamped in an iron stand and is placed in such a position that a large flame can impinge downwards, at about an angle of 45 degrees, upon the contents of the dish. When incineration is well advanced, the dish is heated from below by another all-iron Bunsen burner. In this way as much as 100 grms. of liver can be incinerated in less than an hour in the open laboratory without the emission of disagreeable fumes. The gray ash is heated with 2 c.c. of strong hydrochloric acid (sp. gr. 1·16) over a low Argand flame until the residue is almost dry, after which 1 grm. of citric acid, 2 grms. of ammonium acetate, and 5 c.c. of water are added, and the liquid heated to boiling for about half a minute over a small Bunsen flame. The contents of the dish are filtered into a very small flask (I use ½ oz.—really 17 c.c.—flasks specially made for me by Messrs. Orme). The contents of the dish are washed on to the filter with a few drops of water, about 2 or 3 c.c. in all being used, and to the filtrate is added 1 drop of a 1 per cent. alcoholic solution of phenolphthalein. A 10 per cent. solution of ammonia is added, drop by drop, until a pink colour appears, then strong acetic acid from a small pipette, first until the pink colour disappears, and then until there is an excess of 0·03 c.c.

At no stage of this process should there be any precipitate or opalescence. The citric acid will prevent precipitation of the iron and of small amounts of calcium phosphate. Hydrogen sulphide solution, freshly prepared and strong, is added, and the mixture is kept warm, *e.g.* on a water-oven, for an hour. A Swedish filter, of 4·0 cm. diameter, is folded and fitted into a glass funnel (2·0 to 2·4 cm. diameter) and placed in a flask. Any sulphides and sulphur are collected on the filter, which is finally washed with a few c.c. of weak hydrogen sulphide water. The small filter, with its light or dark brown precipitate, is transferred to a test tube (5·0 cm. by 1·5 cm.), and from a pipette are added 2 c.c. of the following mixture:—Hydrogen peroxide (10 vols), 50 c.c.; dilute sulphuric acid (50 per cent. H_2SO_4 W/W), 10 c.c.; methylated spirit (64 O.P.), 60 c.c. In this mixture lead sulphate is almost insoluble, as 3 c.c. dissolve only 0·003 mgrm. The peroxide is used to oxidise the sulphides to soluble copper sulphate and insoluble lead sulphate, respectively.

The tube is placed in a small beaker containing water above the level of the liquid contents of the tube. The beaker is allowed to stand on a water-oven

until the filter contents are quite bleached, after which the whole is cooled and allowed to stand for an hour. The small filter is removed by means of a glass rod and put into the small funnel placed in a half-ounce flask. The tube contents are poured over the filter and the washing completed by means of 1 c.c. of the peroxide mixture. About 5 c.c. of water are added, and the liquid heated to gentle boiling until all the hydrogen peroxide is expelled. It is then cooled, a drop of phenolphthalein solution added, and the process continued as with the filtrate before the addition of hydrogen sulphide, but with the addition of only 0·1 c.c. excess of acetic acid. The volume of filtrate is made up to 10 c.c. in a graduated flask. Small specimen tubes of clear glass make good miniature Nessler glasses; the smallest of these measures 6·0 cm. by 1·2 cm., and, when full, holds 5 c.c.

The standard copper sulphate contains 0·1 mgrm. of copper in 1 c.c. A freshly-made 1 per cent. solution of potassium ferrocyanide serves as the reagent for the copper. One drop of this solution gives a distinct pink colour with 0·01 mgrm. of copper added in a blank test made as above. For comparison, it is advisable to prepare a blank, with the use of 3 c.c. of the peroxide, with boiling, etc.

The Small Filter and Contents.—Two c.c. of a 40 per cent. (W/V) solution of ammonium acetate are heated to boiling in a small test-tube, the contents poured over the filter, and the filtrate collected in a ½-oz. flask. The filter is washed with about 3 c.c. of hot water. The usual procedure with phenolphthalein and ammonia, etc., then gives a liquid containing a small excess of acetic acid. The solution is made up to 10 c.c., and hydrogen sulphide water is added to 5 c.c. in the small tube. A blank with 2 c.c. of the ammonium acetate, etc., and hydrogen sulphide, a comparison is made with a lead nitrate solution containing 0·1 mgrm. of lead in 1 c.c. In this way 0·005 mgrm. of lead can be determined.

VISCERA, FLOUR, BREAD, ETC.—Human and animal organs, particularly the liver, yield rather large amounts of ash containing much calcium phosphate and carbonaceous matter. The above process, although suitable for beverages, requires modification when applied to materials leaving much phosphatic ash. I found the following to be a satisfactory way of solving the difficulty: Two separate 100 grms. portions of human liver were taken, and to one was added 0·25 mgrm. of lead and 0·25 mgrm. of copper. To the ash in each case was added 5 grms. of the following mixture:—Potassium carbonate, 60; sodium carbonate, 30; and sodium peroxide, 10 parts. After being ground and thoroughly mixed with a small pestle the powder was transferred to a platinum crucible, 42 mm. by 35 mm. wide, and by means of 2 or 3 more grms. of the mixture, the contents of the dish were rinsed into the crucible. The crucible, covered with its platinum lid, was heated over a Bunsen blast flame, and the contents were kept in a state of fusion for about 20 minutes. After cooling, the crucible contents were boiled with a little (not more than 60 c.c.) water until completely disintegrated. Filtration then gave a liquid containing the whole of the phosphate and silicate as alkaline salts. No indication of lead sulphide or copper sulphide was obtained after acidification and addition of hydrogen sulphide.

Sometimes, however, a small amount of these metals may be thrown down; in that case all that is necessary is to collect the sulphides on the same filter as that used for the lead sulphide and copper sulphide obtained from the insoluble residue. This residue is free from carbon (through the action of the sodium peroxide), and consists of the carbonates of calcium and magnesium, with some ferric and aluminic compounds, and, of course, with any (or, indeed, usually all) of the lead and copper, now present as carbonates and oxides.

The filter and contents are incinerated, the ash dissolved in 2 c.c. of strong hydrochloric acid, and the procedure described above closely followed.

The following results illustrate the degree of accuracy of the method:

		Liver.	
		Blank. Mgrm.	With 0·25 mgrm. of lead and 0·25 mgrm. of copper. Mgrm.
Lead found	.. .. ..	0	0·20
Copper ,,	.. .. ..	0·15	0·38=0·23 Cu.
Or in parts per million.		Lead.	Copper.
Added	.. ..	2·5	2·5
Found	.. ..	2·0	2·3
Error	.. .. ..	−0·5	−0·2

CITY AND COUNTY ANALYST'S OFFICE, BRADFORD. F. W. RICHARDSON.

THE REMOVAL AND DETERMINATION OF NITRITES IN SEWAGE EFFLUENTS AND WATERS.

As the result of numerous experiments it appeared that nitrites could be removed easily and efficiently by merely boiling the slightly acidified liquid; and that when distilled off completely they could be collected and determined in the distillate. (ANALYST, 1926, **51**, 405; 1927, **52**, 132.)

In the recently published Ministry of Health account of "Methods of Chemical Analysis as applied to Sewage and Sewage Effluents," a footnote appears on p. 11 to the effect that after "reduction from 100 c.c. to 25 c.c.—apparently under similar conditions—"much nitrite remained."

It is somewhat difficult to understand how such widely different findings could arise over such an apparently simple determination. An unsuccessful attempt was made to obtain further details of the official process used; eventually it transpired that the results had been copied from the Fourth Report of the Royal Commission, Appendix V, pp. 33–35.

Reference to this Report discloses three important facts concerning this determination: (1) After certain preliminary investigations had been made the process was regarded as efficient. (2) Later, a radical change of opinion is recorded, based (presumably) on a series of results characterised by an almost uniform loss of only 50 per cent. of the total nitrous nitrogen after being heated to incipient ebullition; although the original content varied from 0·02 to 0·67 part per 100,000. (3) Kjeldahl determinations on the boiled and unboiled liquid failed to supply the necessary nitrite correction.

A careful examination of the above results suggests their highly improbable nature, owing to the existence of some serious error. The term "incipient ebullition" is somewhat vague; if the process is to be effective, some period of ebullition seems reasonably essential, as the following comparable determinations clearly indicate:

	Amount of nitrous nitrogen. (Parts per 100,000.) (200 c.c. taken.)	Nitrous nitrogen which remained after the sample was: Heated to boiling. Per Cent.	Boiled 2 minutes. Per Cent.	Boiled ·5 minutes. Per Cent.
(1)	2·0	58	9	2 to 3
(2)	0·20	77	25	1
(3)	0·02	65–80	10	nil
(4)	0·02	90–95	52	6

Metaphenylenediamine was the reagent used, except in series 4—which is a duplicate determination of the previous one; in this, the naphthylamine sulphanilic acid reagent was substituted, as it is much better suited to the determination of small amounts.

Consideration of the above results adequately disposes of the idea that there is any difficulty in the removal of nitrous nitrogen by this method; the reduction in volume occasioned by 5 minutes' boiling was about 30 c.c., or 15 per cent.

It is only necessary to account, if possible, for the Royal Commission results; unfortunately, having failed to obtain further details of the exact procedure adopted, I can only surmise the origin of these errors. The radical change of opinion already noted was probably coincident with some slight modification of the process. Can it be that these liquids were now distilled and the nitrites determined in the distillates? If this occurred—and one cannot seriously entertain the idea that the boiled residues were repeatedly examined with the results recorded—the whole difficulty disappears. The 50 per cent. loss observed will now represent finality, coincident with the total removal of the nitrous nitrogen, as half the original nitrite is lost during distillation.

When a solution containing 0·001 grm. and upwards of nitrous nitrogen is distilled in a glass apparatus, brown fumes of nitrogen tetroxide appear in the condenser tube; with precautions these may be absorbed in NaOH and if large in amount may be titrated acidimetrically with reasonable results. It is important, however, to notice that, in spite of this agreement, the amount of nitrous nitrogen in the distillate is only half the amount taken and, as the equation—$N_2O_4+2NaOH=NaNO_2+NaNO_3+H_2O$—indicates, both nitrites and nitrates appear in the distillate. Similar results are obtained when weak solutions are distilled in the ordinary manner without absorbent. Ineffective attempts were made to increase the nitrous yield by the use of carbon dioxide and coal gas; although the latter has often been recommended for similar purposes, its use with small quantities seemed undesirable. Since attention has not been specially directed to this loss in the usual treatises devoted to sewage analysis, this note may serve a useful purpose.

Although the above reaction is well known, it is not unnatural to expect the whole of the nitrites in the distillate; this result Raschig considers characteristic of the *iso* form (see Thorpe, *Dict. Applied Chem.*, 1912, p. 688), and gives $N_2O_4+2NaOH=2NaNO_2+H_2O+O$ as a distinctive reaction for this substance.

J. W. Haigh Johnson.

Walton, Wakefield.

Legal Notes.

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

COMPLETION OF A SALE.

On March 26th an appeal was heard in the King's Bench Divisional Court before the Lord Chief Justice and Justices Avory and Branson. The appellant, an inspector under the Food and Drugs Act, asked that the judgment of the Stroud justices in refusing to convict a trading firm should be set aside.

Mr. Bosanquet, K.C., for the appellant, said that the inspector had gone into the respondent's shop and asked for a tin of golden syrup, and was supplied with a tin labelled "table syrup," which was sold at 8½d. The assistant, on being told that the syrup was purchased for analysis, and that he had not supplied golden syrup, at once said that he had made a mistake and offered a tin which was labelled "golden syrup." The manager also informed the inspector that the article was not sold as "golden syrup," and when the article was divided into three parts he refused to accept one of them. The manager had protested that up to that point there had been no sale, for the inspector had not paid for the article.

The whole point in the case was whether the sale had been completed. The appellant's contention was that when he asked for golden syrup and was handed "table syrup" a sale was completed, but the respondents replied that the appellant was informed of the error before completion of the sale. The Stroud magistrates had accepted the view of the respondents and had dismissed the case.

Sir H. Curtis Bennett, K.C. (for the respondents) laid stress upon the point that as soon as the assistant had handed the tin of "table syrup" to the inspector he had pointed out his mistake. There had been no deceit, and no attempt to foist upon the customer something for which he had not asked. There had been no complete sale until the article was paid for.

Mr. Bosanquet replied that the sale was completed as soon as the syrup was handed to the inspector; it was immaterial whether payment was made at the time or not.

The Lord Chief Justice said that there was a conflict of evidence as to the exact time payment was made for the syrup, but, for the purposes of this case, that did not matter. It was admitted that golden syrup was asked for, and that something not golden syrup was handed over. The Act said, "No person shall sell," and the question was whether so much was done here as to bring the transaction into the provision of the Act. There was no doubt that a cash transaction was contemplated, and when the goods were supplied the seller expected to be paid. It seemed, therefore, for the purpose of legislation, that there was a sale by the respondent to the appellant, and a contract for the sale of the material handed by the shop assistant to the inspector. The fact that the money was not paid at the same second of time as the appellant handled the syrup did not matter. It was said that the assistant had made an error, but no reference to that error was made until the inspector had declared himself.

The Court allowed the appeal with costs and referred the case back to the justices with instructions to convict.

RUM AND COFFEE.

On April 8, a trading firm was summoned at Bradford for having sold rum and coffee which was found to be deficient in rum.

Evidence was given that an inspector under the Food and Drugs Act purchased a cup of rum and coffee which was found on analysis to contain no rum, but only a trace of rum essence, which merely gave the flavour and taste of rum without containing any alcohol.

The solicitor for the defence, said that, unfortunately, the defendants had omitted to avail themselves of a warranty, but the wholesalers who supplied them took the whole responsibility upon themselves. Their explanation was that the consignment of rum and coffee had been kept in stock longer than usual, and the rum had evaporated.

The Bench imposed a fine of 40s.

Ministry of Agriculture and Fisheries.

STATUTORY RULES AND ORDERS, 1929, No. 1115.*

AGRICULTURAL PRODUCE (GRADING AND MARKING), ENGLAND.

THE AGRICULTURAL PRODUCE (GRADING AND MARKING) (MALT FLOUR AND MALT EXTRACT) REGULATIONS, 1929, DATED NOVEMBER 29, 1929, MADE BY THE MINISTER OF AGRICULTURE AND FISHERIES AS TO GRADE DESIGNATIONS AND GRADE DESIGNATION MARKS FOR MALT FLOUR AND MALT EXTRACT.

In exercise of the powers conferred on him by the Agricultural Produce (Grading and Marking) Act, 1928, the Minister of Agriculture and Fisheries hereby makes the following regulations:—

1. Grade designations to indicate the quality of malt flour produced from barley and/or wheat grown in England and Wales shall be as follows:—

ALL-ENGLISH MALT FLOUR (WHITE BREAD).
ALL-ENGLISH MALT FLOUR (BROWN BREAD).

and the quality indicated by such grade designations shall be deemed to be as described in the First Schedule hereto.

2. Grade designations to indicate the quality of malt extract produced from barley grown in England and Wales shall be as follows:—

ALL-ENGLISH (PHARMACEUTICAL) MALT EXTRACT.
ALL-ENGLISH (BAKERS') MALT EXTRACT (WHITE BREAD).
ALL-ENGLISH (BAKERS') MALT EXTRACT (BROWN BREAD).
ALL-ENGLISH (VETERINARY) MALT EXTRACT.

and the quality indicated by such grade designations shall be deemed to be as described in the Second Schedule hereto.

3. A grade designation mark shall be any one of the grade designations specified in regulations 1 and 2 above, associated with the words "Empire Buying Begins at Home" and with the following mark, namely, a map of England and Wales in silhouette with the words "Produce of England and Wales" inscribed in a circle placed centrally in the map within which circle is a design representing the Union Jack and which is more particularly described in the Fifth Schedule hereto.

4. These regulations may be cited as the Agricultural Produce (Grading and Marking) (Malt Flour and Malt Extract) Regulations, 1929.

In Witness whereof the Official Seal of the Minister of Agriculture and Fisheries is hereunto affixed this twenty-ninth day of November, 1929.

(L.S.) CHARLES J. H. THOMAS.

* H.M. Stationery Office. Price 2d. net.

SCHEDULE I.

MALT FLOUR PRODUCED FROM BARLEY AND/OR WHEAT GROWN IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS.

Grade Designation.	Definition of Quality.				
	Particular Characteristic.	Common Characteristics.			
	Diastatic Activity (or Lintner Value).*	General.	Special.		
			Moisture Content.	Ash Content.	Fibre Content.
All-English Malt Flour (White Bread).	Not less than 40.	The flour shall be the pure product of cleaned malted grain and be sound, free from taint or objectionable flavour, of good keeping quality, and otherwise shall comply with the requirements of the Food and Drugs (Adulteration) Act, 1928.	The moisture content, as determined by drying out a weighed quantity of the flour at 100° Centigrade, shall not exceed 10 per cent. of the total weight.	The ash content, as ascertained in a muffle furnace, shall not exceed 1·3 per cent. by weight of the total flour.	The fibre content, as determined in the manner prescribed in Schedule IV, shall not exceed 2·5 per cent. of the total weight of flour.
All-English Malt Flour (Brown Bread).	No fixed minimum.				

SCHEDULE II.

MALT EXTRACT PRODUCED FROM BARLEY GROWN IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS.

Grade Designation.	Definition of Quality.			
	Particular Characteristic.	Common Characteristics.		
	Diastatic Activity (or Lintner Value)*	Protein Content.	Special.	General.
All-English (Pharmaceutical) Malt Extract.	Not less than 25	The amount of soluble protein, as ascertained by multiplying the nitrogen present (other than ammoniacal or nitric nitrogen, if any) by 6·25, shall be not less than 5 per cent. of the total weight.	The Specific Gravity shall be not less than 1·4.	The extract in each case shall be the entire and pure product of commercially sound, clean, malted grain, and shall otherwise comply with the requirements of the Food and Drugs (Adulteration) Act, 1928.
All-English (Bakers') Malt Extract (White Bread).	Not less than 40.			
All-English (Bakers') Malt Extract (Brown Bread).	No fixed minimum.			
All-English (Veterinary) Malt Extract.	Not less than 15.			

* The diastatic activity (or Lintner Value) shall be determined in the manner prescribed in Schedule III.

SCHEDULE III.

METHOD OF DETERMINATION OF DIASTATIC ACTIVITY (OR LINTNER VALUE).

The following detailed instructions shall be carefully observed.

Soluble Starch.

Purified potato starch is digested with dilute hydrochloric acid of a specific gravity of 1·0370 in the proportions of 1 lb. of starch to 1 litre of dilute acid at a temperature which ought not appreciably to exceed 60° F. for seven days, and the mixture should be thoroughly shaken daily. At the end of this time the starch is washed thoroughly by decantation, at first with tap water until the wash water reacts very faintly acid with litmus paper. It is then washed four times with distilled water. A small portion of the starch is then collected on a filter paper on a small Buchner funnel and pumped as dry as possible. Ten grms. of this moist starch are taken and dissolved in 200 millilitres of boiling neutral distilled water contained in a porcelain dish. Two or three drops of alizarin cream are added as indicator and $N/10$ sodium hydrate added from a burette until the neutral point is reached.

The amount of sodium hydrate required to neutralise the whole bulk starch used is calculated from this result, and 25 per cent. extra to compensate for the moisture in the starch tested is added to the bulk, and the whole shaken up thoroughly and allowed to stand 12 hours. It is then washed three more times with distilled water, collected on a paper in a Buchner funnel and pumped as dry as possible. It should then be transferred to new unglazed porous plates and dried at a moderate temperature (110° F.) as quickly as possible. When the moisture content has been reduced to about 15 per cent. the starch is ground in a porcelain mortar and rubbed through a fine hair sieve.

Distilled water is used in making up all solutions, and rinsings after washing apparatus.

Soluble Starch Solution.

Twenty grms. of soluble starch are weighed out and worked into a cream with water and poured into about 600–700 ml. of boiling water contained in a 1,500 ml. boiling flask, and the boiling continued for two minutes after returning to boil; cool to 70–75° F. Shake frequently to prevent the formation of a skin, add 20 ml. of the acetate buffer solution and make up to 1 litre with water and thoroughly mix. (Ten ml. of this solution should not reduce 0·1 ml. of Fehling's Solution.)

The acetate buffer solution is prepared by dissolving 68 grms. of sodium acetate ($CH_3COONa.3H_2O$) in 500 ml. of normal acetic acid and making up to 1 litre with distilled water. (Whatever amount of starch solution is required is made up in 1 litre lots to ensure similar conditions of boiling, etc., fresh solutions being prepared for each day's determinations. 200 ml. graduated flasks are used for the subsequent digestion and two or more are employed for each syrup under test, according to the knowledge of approximate diastatic activity.)

Measure into each flask 100 ml. of soluble starch solution and immerse the flasks, suitably supported, in a water bath kept constant at 70° F.

Malt Extract (Syrup) Solution.

Prepare a 5 per cent. solution—weigh out 10 grms. in a porcelain dish, break down with cold water (on no account must heat be used to assist in weighing or bringing into solution), stirring with a glass rod—transfer into a 200 ml. graduated flask, make up to the mark with water at 60° F.—shake well to ensure solution. Weaker solutions also made up at 60° F. are prepared from this.

Malt Extract (Flour) Solution.

A 5 per cent. extract solution is prepared by placing 10 grms. of flour into a beaker, adding 200 ml. of water at 70° F. and thoroughly stirring the mixture. The mash is allowed to stand for three hours at a temperature of 70° F. and stirred at intervals of half-an-hour. At the end of three hours the mash is filtered quite bright through a good quality filter paper. The first 25 ml. passing through the filter are discarded and the remainder used for the purpose of making determinations, similar methods being adopted as in the case of Malt Extract (Syrup) Solution.

Method of Starch Conversion.

The necessary quantities measured at 60° F. are added to the digestion flasks now ready at 70° F. (In the case of average extracts using a 2½ per cent. solution from 1·2 to 1·6 ml. will represent a suitable amount.) It is essential that the malt extract solutions be used as soon as possible after making up. The extract (syrup) solutions should not be filtered.

A narrow bore pipette (N.P.L. Standard) having a good clearance tip is used to add the extract solution, after which the contents of the flask are well shaken. The time is noted, and a

short scale (60–90° F.) large degrees thermometer (N.P.L. Certificate) is inserted into each flask and they are maintained for *exactly* one hour at 70° F. Then to each flask are added 20 ml. *N*/10 sodium hydrate solution, care being taken to wash down the thermometer and also to allow the alkali to flow over the inner surface of the neck of the flask. The flasks are thoroughly intermixed, cooled, made up to 200 ml. at 60° F. with water, and well shaken. This solution, referred to below as *the conversion solution*, is titrated against 5 ml. quantities of Fehling's solution, using methylene blue solution as an internal indicator.

Fehling's Solution.

This is prepared by well mixing equal volumes of the component solutions Nos. 1 and 2 as given below and measured into a dry flask by means of a pipette. A 1 per cent. solution of methylene blue is used as an indicator. The Fehling's solution should be prepared fresh for each day's determinations—the 5 ml. required for each titration being measured at 60° F. from a standard burette in preference to using a pipette.

Component Solutions :—

1. Copper sulphate solution containing 69·28 grms. $CuSO4$, $5H_2O$ dissolved in 1 litre. This solution is standardised against standard invert solution and adjusted if necessary. (1 ml. Fehling's solution corresponds to ·005066 grm. invert sugar.)

2. Rochelle salt 346 grms.
Sodium hydroxide 130 grms. } Dissolved in one litre of water.

Method of Titration.

Two burettes are required; one is filled with the freshly mixed Fehling's solution and the other with starch conversion solution. Five ml. of Fehling's solution are measured from a burette into a 200 ml. round-bottomed flask and raised to boiling point, the flask being meantime rotated while heating over a naked flame. The conversion solution is then run into the boiling liquid in small amounts from the burette, commencing with 5 ml. After each addition of solution the mixture is boiled, the liquid being kept rotated. When the blue coloration begins to disappear the solution is added in smaller quantities, and when it seems from the bright red colour imparted to the boiling solution by cuprous oxide that the copper is almost reduced, from two to three drops of methylene blue indicator are added to the boiling flask, and the titration continued with small quantities of solution, say 0·5 to 0·1 ml., or drop by drop until the blue colour just disappears. (The indicator is not added until the neighbourhood of the end-point has been reached, as the final change is very rapid. The complete decolorisation of the methylene blue is indicated by the whole reaction liquid, in which the cuprous oxide is continually being churned up, becoming bright red or orange in colour. To ensure that this point has been reached, the flask is held against a sheet of white paper and if the indicator is completely decolorised there should be no blue tint at the edge of the liquid. The boiling process must be sufficiently continuous to prevent air obtaining access to the flask and so causing oxidation of the indicator.)

A first titration to obtain approximate results is followed by a second, or third, if necessary, to establish the end-point accurately. A confirmatory titration should be carried out in every case.

Method of Calculating Diastatic Activity (or Lintner Value).

The diastatic activity is calculated as shown below from results obtained with conversion solutions which require between 20–26 ml. to reduce 5 ml. of Fehling's solution. Conversions giving above or below this range should be repeated by the addition of lesser or greater quantities of the diluted malt extract solutions, as the case may be. If the original 5 per cent. malt extract (syrup) solution has been aerated in any way, filtered for colour, or subjected to warm conditions, it will be necessary to reweigh and carry out the dilutions again.

The result is expressed on a 5 per cent. solution according to the following formulæ:—

(*a*) in the case of flour, Diastatic Activity (or Lintner Value) $= \frac{1000}{X \times Y}$.

(*b*) in the case of syrup, Diastatic Activity (or Lintner Value) $= \frac{1000}{X \times Y}$ minus 9.

where X = number of ml. of the 5 per cent. malt extract solution in 100 ml. of the conversion solution,

Y = number of ml. of conversion solution required to reduce 5 ml. of Fehling's solution, and

9 = a constant denoting the assumed equivalent of the reducing sugars present in the malt extract (syrup) used in making the determinations.

(Example:—Conversion performed with 1·6 ml. of 2·5 per cent. malt extract (syrup) solution, and 25·0 ml. of conversion solution required to reduce 5 ml. of Fehling's solution.

$X = 0{\cdot}4$ ml.

$$\text{Diastatic Activity (or Lintner Value)} = \frac{1000}{0{\cdot}4 \times 25{\cdot}0} = (100 - 9) = 91.)$$

(*Notes.*—1. There is a tendency for a film to form on glassware used in starch conversions, and all apparatus used for this purpose should be cleaned with warm sulphuric acid containing a little chromic acid and subsequently thoroughly washed.

2. When carrying out these determinations, it will be found advantageous to make simultaneously control determinations on a malt flour or syrup of known diastatic activity.)

SCHEDULE IV.

Determination of Fibre-content.

Two or three grms., accurately weighed, shall be extracted with petroleum spirit, b.pt. 40–60° C. in an extraction apparatus, or at least three times by stirring, settling and decantation, and the dry residue transferred to a conical 1,000 ml. flask. The material must not be further ground during extraction. A volume of 200 ml. of a solution containing 1·25 grms: of sulphuric acid (H_2SO_4) per 100 ml. measured at ordinary temperature and brought to boiling point, shall be added to the flask and heated. The contents of the flask must come to boiling within 1 minute and the boiling throughout must be gentle and continuous for exactly 30 minutes, the original volume being maintained. The flask shall be rotated every few minutes in order to mix the contents and remove particles from the sides. At the end of 30 minutes the flask shall be removed and the contents poured at once into the shallow layer of hot water remaining in a funnel fitted with a pump-plate or alternatively into the similar layer remaining in a Buchner funnel. The funnel shall be prepared by cutting a piece of cotton cloth or filter paper to cover the holes, so as to serve as a support for a disc of ordinary filter paper; boiling water shall be poured into the funnel and allowed to remain until the funnel is hot, whereupon suction is applied. The experiment shall be discarded if the time of filtration of the bulk of the 200 ml. exceeds 10 minutes. The residue shall be washed with boiling water until the washings are free from acid. The residue shall then be washed from the filter paper back into the flask with a volume of 200 ml. of a solution of sodium hydroxide, containing 1·25 grms. of sodium hydroxide (NaOH) per 100 ml. free or nearly free from sodium carbonate, measured at ordinary temperature, and brought to boiling point. The contents of the flask shall be boiled for exactly 30 minutes, the precautions given for the treatment with acid being observed. At the end of 30 minutes the flask shall be removed and its contents immediately filtered through an ordinary filter paper. The residue collected in the filter paper shall be washed with boiling water, then with a solution of 1 per cent. hydrochloric acid and again with boiling water until free from acid. The residue shall then be washed twice with 95 per cent. alcohol, and three times with ether. The residue shall then be transferred to a dried weighed ashless filter paper, dried at about 100° C. in an oven and weighed in its weighing bottle until constant in weight. The ash of the paper and contents shall be determined by incineration at a dull red heat. The weight of ash shall be subtracted from the increase of weight found on the paper and the difference shall be reported as fibre.

Lead Tetra-Ethyl in Motor Spirit.

FINAL REPORT OF THE DEPARTMENTAL COMMITTEE.*

THE final report of the Departmental Committee, appointed in 1928 by the Minister of Health, to inquire into the possible danger to health arising from the use of lead tetra-ethyl in motor spirit has been issued. It confirms the interim report issued in 1928, namely, that, so long as adequate precautions are observed, there are no reasons for prohibiting the use of this type of motor spirit.

The Committee heard the evidence of several scientific witnesses, including Dr. H. E. Armstrong, Dr. Roche Lynch, and Dr. Kehoe, who was responsible for much of the scientific work undertaken in the United States by the Ethyl Gasoline

* H.M. Stationery Office. Price 1s. net.

Corporation. Investigations were also carried out by the Committee's experimental staff, particularly as to the effect of inhaling the vapour when spilling occurred in garages.

DETECTION OF LEAD IN URINE.—It has been found in the United States that normal urine contained minute quantities of lead, but as the Committee was not satisfied that the method of detection used was sufficiently accurate, a new and more refined method was devised, which could be used with biological material in general.* The results were in agreement with those of the American chemists, and showed that normal urine from the male contained on the average 0·04 mgrm. of lead per litre.

LEAD IN DUST OF STREETS AND GARAGES.—The proportion of lead in samples of dust collected in London and neighbouring country districts varied from *nil* to 3·3 per cent. In the view of the Committee the risk of chronic plumbism arising from the daily inhalation of dust or fumes over a long period is remote, and it is pointed out that the lead content in the settled dust of factories using lead is much greater than in garages. The value of the experiments, however, was lessened by the fact that no sample of dust could be obtained from a garage using ethyl petrol exclusively.

CONCLUSIONS.—The principal conclusions at which the Committee arrived are, briefly expressed, as follows:—

1. Urine, in normal conditions, contains a minute quantity of lead, the proportion being less in persons who live in the country. Excretion of lead is caused partly, if not mainly, by inhaling dust containing lead. On an average there is a fairly close relation between the degree of exposure to lead and the proportion of lead in the urine.

2. No evidence has been found to indicate that the settled dust in a garage where ethyl petrol is regularly used for *some* cars contains more lead than that of garages where this fuel is not employed.

3. Lubricating oil from the crank cases of cars using ethyl petrol contains a small proportion of volatile lead; the proportion of non-volatile lead associated with the insoluble "carbon" in the oil is significant. Deposits scraped from the cylinder heads, pistons, and exhaust systems of the engines contain a negligible quantity of volatile lead.

4. Oily deposits from the combustion chamber and exhaust pipes of cars run on ethyl petrol are unlikely to cause serious contamination of any water supply; deposits free from oil will have no serious effect on a water supply of a moderate degree of hardness, but the contamination of a soft water supply by oil-free deposits might be more serious.

5. Risks to health from spilling large quantities of ethyl petrol appear to be slight; if adequate ventilation exists the risk from the spilling of small quantities appears to be negligible. Garages should be efficiently ventilated and spilling should be avoided.

6. It is improbable that pedestrians would inhale a dangerous quantity of lead when "puffs" are blown out of the exhaust pipes of motor vehicles during the acceleration of their engines.

7. The risk from absorption of lead tetra-ethyl owing to contact of ethyl petrol with the skin is so small as to be negligible.

RECOMMENDATIONS.—The Committee advised that no legislative action should be taken so long as the precautions previously advocated are secured by the terms of the contract between proprietors and vendors. These are:

1. That cans and pumps should be labelled to indicate the presence of lead in the fuel and to warn the user to avoid spillage and not to use the fuel for purposes other than motor fuel.

2. That the fuel should be dyed as an additional check against its use otherwise than as motor fuel.

3. That the amount of lead tetra-ethyl in the fuel sold for ordinary commercial purposes should not exceed 1 part in 1,300 parts by volume, or about 1 in 650 by weight.

* *Cf.* Francis, Harvey and Buchan, ANALYST, 1929, **54**, 725.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Reaction between Pectin and Cow's Milk. G. H. Joseph. (*J. Soc. Chem. Ind.*, 1930, **49**, 159–160T.)—Fresh cow's milk, pasteurised, separator-skimmed or homogenised milks containing 0·2 to 0·3 per cent. or more of added pectin coagulates in 10–30 minutes, whereas evaporated, condensed or powdered milk diluted to normal concentrations does not coagulate, and with goat's milk coagulation is slow and incomplete. The coagulate is very fine grained and light coloured with fresh cow's milk, but rather coarse and fluffy with homogenised milk. The *p*H of the fresh milk (6·6) had to be lowered to between 5·3 and 5·4 before coagulation occurred with acid, but in presence of pectin the *p*H may be as high as 6·5. The ash content of the coagulating pectins varied from 0 to 5 or 6 per cent. An analysis of the coagulum from a system containing 0·8 per cent. of pectin showed it to contain about 78 per cent. of the proteins and 16 per cent. of the lactose of the original milk, and all the added pectin. Sodium bicarbonate (0 to 0·4 per cent.), sodium citrate (0 to 0·15), sodium sulphate (0 to 0·5), potassium dihydrogen phosphate (0 to 1), and sodium dihydrogen phosphate (0 to 0·6 per cent.) had no effect on the coagulation. The properties of casein sols were also investigated. Apparently coagulation only takes place when pectin, casein and calcium ions are present together, but coagulation occurs when the calcium ions are removed by any other method than by the oxalate ion. D. G. H.

Colour Reaction of the Proteins of the Wheat Corn. E. Rabaté and J. Fleckinger. (*Compt. rend.*, 1930, **190**, 748–750.)—A mixture of a cold solution of potassium bromide with an equal volume of pure sulphuric acid gives a red colour if evaporated with traces of copper salts (Denigès). Positive reactions were obtained with sections of a wheat corn, irrespective of whether it had been treated with copper sulphate (against *Tilletia caries*) or not. The cotyledons gave the most marked reactions, the protein and diastase layers a fainter colour, whilst a violet tint developed in the albumin only after some time. Separate experiments with sulphuric acid, bromine and hydrobromic acid indicated that the colorations produced by the different portions of the grain are due only to the copper retained by the proteins. J. G.

Pollen Analysis of Honey. C. Briebel. (*Z. Unters. Lebensm.*, 1930, **59**, 63–79.)—A series of photomicrographs of the pollen grains found in honey is given for use in determining if the honey is of native or foreign production. An aqueous solution of the honey (1 : 2) is employed, and a magnification of 175 (sometimes 350) diameters is convenient. Since the pollen grains change in shape considerably in

the honey solution, owing to absorption of water, those from the comparison flowers must be soaked in honey solution of the same strength for 24 hours. This may be done on the microscope slide, the cover-slip being sealed with molten paraffin wax. This procedure has the advantage that the pollen appears bright and is not easily crushed. A collection of different pollens may be made by gathering the flowers just before they are completely open, drying them in the air, and storing them in paper bags. If the grains are to be photographed they should be treated with a fat solvent such as ether before being soaked in the honey solution. T. H. P.

Detection of Fruit Wine in Grape Wine by the Sorbitol Process. G. Reif. (*Z. Unters. Lebensm.*, 1930, **59**, 99–104.)—When applied to a sweet apple wine the sorbitol reaction with benzaldehyde and sulphuric acid (*cf.* Werder, ANALYST, 1929, **54**, 476) gave negative results, although with a dry wine from the same source a positive test was obtained. The failure of the reaction in the former case is due to the presence of sugars, different types of which exert varying influence. If true sugars alone are in question, they may be removed from the urine by fermentation with pure cultures of wine yeasts after the alcohol has been removed. Starch sugar and starch syrup, owing to their content of dextrin, have a marked inhibiting effect on the reaction. To eliminate the dextrin, the wine, freed from sugars by fermentation, is evaporated in a vacuum, and the residue gently boiled for a long time with two successive quantities (20 c.c.) of absolute alcohol. The combined alcoholic extracts are evaporated as completely as possible in a vacuum, and the syrupy residue is mixed with a few drops of water and treated with benzaldehyde (0·2–0·25 c.c.), and at least 1 c.c. of sulphuric acid (1 : 1).

T. H. P.

Arachidonic Acid in Lard. J. B. Brown and E. M. Deck. (*J. Amer. Chem. Soc.*, 1930, **52**, 1135–1138.)—Four samples of lard from different packing houses were examined for arachidonic acid by converting the fatty acids into the methyl esters and isolating the methyl octobromo-arachidates. They contained 0·31 to 0·4 per cent. of the acid. This was roughly proportional to the iodine values of the lards. The percentage of acid was calculated by dividing the polybromide number of the ester by 77·6, the polybromide number of pure methyl arachidonate, and multiplying by 100. Two samples yielded ether-insoluble bromine addition products which were probably mixtures of α-palmito-distearin and a glyceride of octobromo-arachidic acid. D. G. H.

Fatty Acids of Nutmeg (Mace) Butter and of Expressed Oil of Laurel. G. Collin and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1930, **49**, 141–143T.)—Nutmeg (*Myristica officinalis*) butter with iodine value 61, unsaponifiable matter 17·0 per cent., and mean equivalent of mixed fatty acids 246·3, gave 25 per cent. of steam-volatile essential oils and 75 per cent. of fatty residue. The separated fatty acids contained 71·0 per cent. of solid acids and 9·5 of liquid acids, with 19·5 of resins. The percentage composition of the fatty acids was: Lauric 1·5, myristic 76·6, palmitic 10·1, oleic 10·5, linolic 1·3. The butter conforms with the general rule of even distribution of the fatty acids between the glycerides of kernel fats.

The crude kernel fat of *Myristica malabarica* gave about 60 per cent. of refined fat with saponification equivalent 280 and iodine value 77. The mixed fatty acids, as separated, contained 43·1 per cent. of resinous matter, the percentage composition after removal of the resin being: Myristic 30·2, palmitic 13·3, other saturated acids 2·4, oleic 44·1 and linolic 1·0. This fat appears to furnish an exception to the principle of even distribution of the fatty acids in the glycerides of the kernel.

Crude expressed oil of laurel is dark-green and semi-solid, with saponification equivalent 269·8, acid value 9·0, iodine value 86·4, unsaponifiable matter 6·2, mean molecular weight of fatty acids 249·5. The percentage composition of the mixed fatty acids of the refined oil was: Lauric 35·0, palmitic 9·7, oleic 36·6, linolic 18·7, the estimated equivalent being 244·1, and the iodine value 66·9. The composition represents a heterogeneous mixture, probably owing to the presence of both seed and pericarp fats in the sample examined. T. H. P.

Dika Fat (Irvingia Butter). G. Collin and T. P. Hilditch. (*J. Soc. Chem. Ind.*, 1930, **49**, 138–139T.)—Nuts of *Irvingia Barteri* from Nigeria consisted of 82 per cent. of a very thick, tough shell, enclosing thin, flat kernels (18 per cent.), which contained 69 per cent. of fat having saponification equivalent 233·9, iodine value 9·1, unsaponifiable matter 1·05 per cent., and m.pt. 41–42° C. The mixed fatty acids had the mean equivalent 220·3 and m.pt. 37·5–38° C., and consisted of lauric (38·8), myristic (50·6), and oleic (10·6 per cent.). The fat contained 79 per cent. of fully-saturated glycerides, and in the mixed saturated-unsaturated glycerides there were present 1·3 mols. of saturated acids per mol. of unsaturated acids, so that the glyceride structure is of the uniform, evenly-distributed type apparently characteristic of most kernel fats. No evidence of the presence of simple triglycerides was detected, and the fat appears to be made up mostly of laurodimyristins and dilauromyristins, its comparatively simple nature and the low molecular weight of the component acids leading to a material of somewhat brittle texture with a comparatively sharp low melting point.

T. H. P.

Pentose and Uronic Acid Content of Orange Albedo and an Arabino-galacturonic Acid derived from Orange Pectin. J. R. Bowman and R. B. McKinnis. (*J. Amer. Chem. Soc.*, 1930, **52**, 1209–1215.)—The simultaneous determination of pentose and uronic acid in orange pectin, is possible because pentoses when boiled with dilute acids give a constant, but not maximum, yield of furfural which distils and can be precipitated with phloroglucinol, whilst uronic acids first yield carbon dioxide to form pentoses, and these in turn yield furfural. The formic acid type of decomposition does not take place to any appreciable extent under the conditions observed. The steam distillation train consists of the steam generator, reaction flask, and condenser filled with fine spongy zinc, kept moist by reflux action from a flask connected with the furfural collection flask. This is fitted with an upright condenser connected with two barium hydroxide containers. The sample and 200 c.c. of 12 per cent. hydrochloric acid are

boiled, the carbon dioxide swept out by suction and eventually determined by titration of the barium hydroxide into which it is passed. Steam is blown through the reaction flask, and by a special device it is possible to sample the distillate without an influx of carbon dioxide. Distillation is stopped half an hour after a practically colourless test is given with aniline acetate paper, and furfural is determined as the phloroglucide without washing with alcohol. Twice as much furfural as carbon dioxide was produced from orange albedo, as also from the arabino-galacturonic acid isolated from it, indicating that an equal proportion of combined pentose and uronic acid, but no free pentose was present. It is probable that some pectins contain both digalacturonic and arabinogalacturonic acids in varying proportions, and results indicate that pectin varies in composition and thus in its products of hydrolysis. D. G. H.

Biochemical.

Colorimetric Method for the Quantitative Determination of Nitrates and Nitrites in Biological Fluids. M. Whelan. (*J. Biol. Chem.*, 1930, **86**, 189–197.)—An accurate method for the determination of nitrates in blood and urine is necessary for complete studies of nitrogen metabolism in patients to whom nitrates are given as diuretics. Various colorimetric methods for the determination of nitrates have been described. Caron (*Ann. chim. anal.*, 1912, **17**, 9) used diphenylamine, but the results were widely variable. Letts and Rea (*J. Chem. Soc.*, 1914, **105**, 1157) replaced diphenylamine with diphenylbenzidene, but the resulting blue colour faded rather rapidly, and colorimetric determinations could not be made. An accurate method for the determination of nitrates and nitrites is now described. It is based on the development of a blue colour by diphenylbenzidine, but the method is substantially new. It has been found possible to get a uniform development of colour under conditions that permit the colorimetric comparison of standard and unknown. The method permits the determination of 0·0003 mgrm. of nitrate nitrogen for each c.c. of material. It has been applied to urine, blood, ascitic fluid, pleural fluid, oedema fluid and saliva, with an average error of ± 2 per cent. The essential elements in control of the development of colour were prevention of rapid fading of colour, control of temperature and removal of protein. The colour develops fairly uniformly and reaches its maximum in about 90 minutes; it does not begin to fade for another 40 minutes. Addition of sodium chloride to the reagent intensifies and stabilises the colour developed. Mercuric chloride is used as a protein precipitant. Full details of the method and necessary precautions are given. Tables show the recovery of nitrate nitrogen added to blood, ascitic fluid and urine, and a comparison of the diphenylbenzidene method with that of Schulze. P. H. P.

Unlaked Blood as a Basis for Blood Analysis. O. Folin. (*J. Biol. Chem.*, 1930, **86**, 173–178.)—The multiplicity of revisions and modifications proposed from time to time for the Folin-Wu system of blood analysis has caused

much confusion among those who wish to apply the methods, and it is therefore not without regrets that the author proposes a radical revision of the Folin-Wu method for the preparation of protein-free blood extracts. Nearly all the points most frequently debated owe their uncertainty to the fact that the blood filtrates include constituents of the disintegrated blood corpuscles. It would be more satisfactory, and should be practicable, to prepare from whole blood aqueous filtrates or extracts which contain the plasma constituents, together with the readily diffusible products of the blood cells, but which are free from the disintegration products of the cells. A new form of blood extract has been developed in connection with a study of the puzzling problem as to why one cannot recover known quantities of uric acid when these are added to blood which is practically free from uric acid. Experiments carried out with the new extract, in comparison with the regular Folin-Wu filtrates, show: (1) There is no material loss of uric acid through adsorption by the protein precipitate, (2) the disappearance of uric acid is due to some inhibiting action by the blood filtrate on the colour development, and (3) both the inhibiting action and the blank due to reactive non-uric acid substances in blood are almost completely eliminated by the new method for removing the blood proteins. For the ordinary preparation of unlaked blood extracts the following solutions are used: (1) A solution containing 15 grms. of anhydrous sodium sulphate and 6 grms. of sodium tungstate per litre, and (2) $\frac{1}{3}$ *N* sulphuric acid. Forty c.c. (8 volumes) of the sulphate-tungstate solution are transferred to a small flask, and 5 c.c. of blood are added, mixed without any rough shaking, so as not to damage the cells mechanically, and allowed to stand, with occasional very gentle shaking, for 5 minutes, or longer. With a pipette 5 c.c. (1 volume) of $\frac{1}{3}$ *N* sulphuric acid are added rather slowly, with constant but gentle mixing, and the mixture is transferred to 15-c.c. centrifuge tubes, and centrifuged for 10 minutes at a moderate speed. The supernatant liquid should be perfectly colourless and clear as water. In this unusual form of blood protein precipitation the blood cells are scarcely, if at all, acted upon by the tungstic acid. There is obtained a mixture of precipitated plasma proteins and shrunken but not disintegrated blood cells. After about 45 minutes, if left standing, the cells begin to disintegrate. Filtration should not be used in place of centrifuging. Over one-third of the total non-protein nitrogen in the Folin-Wu filtrates is represented by unknown substances. This undetermined nitrogen comes largely from the disintegrated blood cells, and most of it, therefore, should fail to appear in the filtrates obtained from unlaked blood. The Folin-Wu method for the blood sugar determination is applicable to the new filtrate. By the addition of 2 per cent. sodium sulphate to the sugar standard, and the use of the method as recently described by Folin (*J. Biol. Chem.*, 1929, **82**, 91), it becomes more reliable than it has ever been. The sugar values found are lower than the values given by the Folin-Wu filtrate, and the non-fermentable "sugar" has practically vanished. The few comparative urea determinations made, so far, indicate that the values obtained from the unlaked blood extracts are substantially identical with those obtained from the Folin-Wu filtrates. P. H. P.

Inheritance Study of the Distribution of Vitamin *A* in Maize. II. Vitamin *A* in Hybrid Red Maize. S. M. Hauge. (*J. Biol. Chem.*, 1930, **86**, 161–165.)—The knowledge that in hybrid corn there are strains which give increased yields, and also possess other desirable qualities, has resulted in increased production of these types of corn until they have assumed an economic importance. Hybrids are produced by crossing yellow and white corn, and also by crossing the red varieties with other strains of corn. The quantities of these hybrids which are available for feeding purposes make it desirable to secure information as to the inheritance of vitamin *A* in relation to colour characteristics of the pericarp and endosperm. Hauge and Trost (*J. Biol. Chem.*, 1928, **80**, 107) made an inheritance study of the distribution of vitamin *A* in F_2 segregating kernels of crosses of yellow dent and white dent corn. They found that vitamin *A* is present only in kernels possessing yellow endosperm. The corn used in their experiments possessed colourless pericarp. These inheritance studies have now been extended to include strains of corn possessing red pericarp, in order to study the possible effect of pericarp colour. The lots of corn used were selected from two hybrid strains, one with colourless pericarp and the other with deep red pericarp. From the ears of corn of the F_2 generation of the cross white dent by yellow dent, equal quantities of (1) F_2 yellow, YYY, and (2) F_2 white, yyy, were selected from each ear. From the ears possessing red pericarp, (3) red grains with yellow endosperm, and (4) red grains with white endosperm were secured from the same ears. A portion of the pericarp was removed from each kernel in (3) and (4), in order to determine the colour of the endosperm. These 4 classes of materials were tested for vitamin *A* on young albino rats. The results show that in hybrid red maize, vitamin *A* is associated with yellow endosperm, and is lacking in the corn grains with pure white endosperm, even when grown on the same ears as those possessing grains with yellow endosperm. These experiments with red grains further substantiate the previous report that there is a close physiological association between vitamin *A* and yellow endosperm character. The colour of the pericarp appears to have no effect on the vitamin *A* content of corn. P. H. P.

Inheritance Study of the Distribution of Vitamin *A* in Maize. III. Vitamin *A* Content in Relation to Yellow Endosperm. S. M. Hauge and J. F. Frost. (*J. Biol. Chem.*, 1930, **86**, 167–172.)—The previous results suggest two possible explanations for the association of yellow endosperm with vitamin *A* formation. If the vitamin *A* content of all types of yellow corn with various degrees of colour intensity is the same, this would suggest the possibility of a catalytic action by the yellow pigments in the formation of vitamin *A*, whereas if the vitamin *A* content parallels the amount of colour character, either the physiological relationship must be very close or the factor acting as vitamin *A* may be the yellow pigment itself. To test this relationship, comparisons have been made of the vitamin *A* content of two classes of Dent corn, YYY and Yyy, possessing as wide a range of yellow endosperm character as possible. The genetic constitution of the endosperm of the two samples is represented as follows: F_1 Johnston County

White Dent × Reid Yellow Dent gave Yyy, two white factors from the female and one from the male; Reid Yellow Dent gave YYY, yellow factors from both parents. The results show that the critical level for the Yyy corn is approximately 15 per cent., whereas that of the YYY corn is about 5 per cent. Seven per cent. of YYY corn gave good growth, whereas it took 20 per cent. of Yyy corn to give comparable results. It is apparent that the carotinoids in corn do not function merely as catalytic agents in the formation of vitamin *A*. The results indicate that the ratio of vitamin *A* content in YYY and Yyy corn is about 3:1. It is concluded that the vitamin *A* content of Dent corn is controlled by ordinary hereditary factors. These are the same as those which govern development of the yellow endosperm. P. H. P.

Vitamin *A* and Carotene. N. Bezssonoff. (*Compt. rend.*, 1930, **190**, 529–532.)—The author (*Revue pathol. végét.*, 1927, **9**, 568; *Bull. Soc. chim. biol.*, 1929, **11**, 1146) has outlined the following method for the isolation from vegetables of a lipoid fraction containing all the vitamin *A* and carotene, but free from chlorophyll. The fresh vegetable juice is mixed with a neutral lead acetate solution; the precipitate obtained, after drying, yields, on extraction with petroleum spirit or benzene, about a quarter of the lipoids present in the vegetable, and this fraction contains vitamin *A* and carotenes. After evaporation of the solvent the residue is dissolved in arachis oil and used for biological tests. A preparation of this kind, obtained from carrots, was given to rats in daily doses of 0·025 and 0·05 mgrm. of lipoid residue, equivalent to about 100 and 200 mgrms. of carrot juice, and the gain in weight of these rats was compared with that of rats given cod-liver oil. All the rats had been given a diet deficient in vitamin *A* for 100 days beforehand. The results are shown graphically and demonstrate that the group of rats given a daily dose of 0·025 mgrm. of residue (equivalent to 0·0021 mgrm. of carotene) grew better than the group receiving 9 mgrms. of cod-liver oil daily. The results and conclusions of other workers are discussed. Others seem to have obtained the same vitamin *A* effect with 0·01 mgrm. of crystalline carotene that the author has shown with 0·025 mgrm. of lipoid substance (containing 0·002 mgrm. of carotene); if the crystalline carotene is pure vitamin *A*, this upsets the hypothesis that among the different carotenes of a plant one only is vitamin *A*. All attempts to isolate an active preparation, free from carotene, from vegetables, have failed. The difficulty in separating vitamin *A* and carotene is not sufficient proof that they are identical, and other explanations of the bond between them are more in agreement with experimental data. They are the selective absorption of vitamin *A* by carotene, its peculiar adherence to the latter, and the existence between them of molecular combinations. P. H. P.

Carotene. I. Oxygen Equivalent Determined with Potassium Permanganate in Pyridine Solution. J. H. C. Smith and H. A. Spoehr. (*J. Biol. Chem.*, 1930, **86**, 87–92.)—This publication is the first of a series on work carried out with the object of describing more accurately the photo-synthetic

apparatus of the plant. Carotene, an unsaturated hydrocarbon, which is universally present in the chloroplasts, though its chemical structure and physiological rôle are as yet not determined, is one of the simplest leaf pigments. Escher (*Zur Kenntniss des Carotins und des Lycopins*, Dissertation, Zurich, 1909, 79) attempted to determine the oxygen equivalent of carotene suspended in water, but found that various treatments yielded different values. His highest value was 42 atoms per mol. of carotene. (The *oxygen equivalent* is defined as the number of oxygen atoms used by 1 mol. of a substance when oxidised with potassium permanganate.) The authors realised the usefulness of the oxygen equivalent in theoretical considerations of chemical structure, and tried to repeat the work of Escher. The first method tried gave results which were of little value. It was decided to use a liquid which would dissolve both carotene and potassium permanganate and would react only very slowly if at all with the permanganate. Pyridine was found to be an excellent solvent for carotene, and reasonably stable when kept with potassium permanganate at temperatures below 40° C. A method has therefore been developed by which the oxygen equivalent of an organic substance may be determined in pyridine solution. The reaction tubes (ordinary soft glass test-tubes) are divided into two groups, A and B. Group A is used for the oxidation of the substance and group B for the controls. To each tube in Group B are added 3·0 c.c. of pyridine, and to each tube in Group A, 3·0 c.c. of pyridine solution containing the substance to be oxidised. Then 10·0 c.c. of a standard pyridine-permanganate solution (pyridine saturated at room temperature with permanganate) are added to all the tubes, which are stoppered with cork stoppers covered with lead foil. Four tubes of each group are put into a constant temperature bath at 37·5° C., and one of each group is titrated immediately to give the initial reading. Details are given of the method of titration against oxalic acid for the determination of the quantity of permanganate reduced, and of the calculations. Tables show that the oxygen equivalent of cinnamic acid has been found to be 4·97, which is in agreement with the theoretical value of 5·00. The oxygen equivalent of carotene was found to be 41·97; this confirms the value 42 previously reported by Escher. Oxidations with permanganate in pyridine solution are not new, but the authors believe this is the first time they have been followed quantitatively. P. H. P.

Vitaminic Activity of Carotene. M. Javillier and L. Émerique. (*Compt. rend.*, **1930**, **190**, 655–657.)—The relation of vitamin *A* to carotene is discussed and, although it is recognised that pure carotene is not the vitaminic substance, the remarkable tenacity with which the *A* factor remains associated with carotene is emphasised. A sample of carotene, prepared from spinach forty years ago, and kept in a sealed tube in an atmosphere of hydrogen, still exerts the physiological activity of vitamin *A*. When administered to rats in doses of the order of 0·01 mgrm. per day per 100 grms. of body weight, it removes the disabilities caused by an avitaminous diet and stabilises the growth curve.

T. H. P.

Feeding Experiments with Activated Ergosterol. I. C. E. Bills and A M Wirick. (*J. Biol. Chem.*, 1930, **86**, 117–128.)—A brief discussion is given of reports by other workers on the action of large doses of irradiated ergosterol. In nearly every case the workers failed to determine the potency of the product which they employed; they stated only the quantity of irradiated ergosterol in mgrms. It must be accepted that while very large doses of activated ergosterol are not immediately toxic, yet relatively enormous doses do produce serious effects. Up to the present, published experiments have been based on short time tests, covering at the most a few months of life in the rat. The potency of irradiated ergosterol varies with the conditions under which activation is performed, values from zero to a million times the potency of average cod-liver oil being obtainable. The material used in most of the experiments now described had a potency prior to dilution of about 400,000 times the over-dosage. The ergosterol intake of the rats receiving the minimum antirachitic dose may therefore be determined as $\frac{1}{16,000,000}$ grm. per day when the food intake was 10 grms.; *i.e.* the modified diet then contained 1 part of ergosterol to 160,000,000 parts of ration. Experiments continued over long periods have been carried out on rats, and composite growth curves show the results. In these experiments, activated ergosterol administered to rats in doses 100 times greater than the minimum antirachitic level showed no effect on general appearance, growth, reproduction, or resistance to respiratory infections; 1000 times over-dosage was just perceptibly harmful, 4000 times over-dosage definitely injurious, and 40,000 times over-dosage strongly toxic. The toxic action was intensified by calcium carbonate, but unaffected or slightly lessened by disodium phosphate. No significant quantity of activated ergosterol was received by rats *in utero*. Nursling rats received in their milk a small amount of vitamin *D* when the mothers were given enormous overdoses. The investigations reported involve some 1200 rats, including second and third generations; the work covers the period from infancy to late maturity. The authors intend to continue the study on the same original rats, keeping them under observation until they die, and later to report on the blood chemistry and tissue changes. P. H. P.

Oxidation of Oils in the Presence of Irradiated Sterols. E. Conture. (*Compt. rend.*, 1930, **190**, 532–533.)—Experiments which have been carried out on the photochemical action of irradiated sterols on the photographic plate have shown the presence of aldehydic products and of active oxygen, probably due to the breaking off of an ozonide formed on the ethylene bonds of the sterol molecule. It was thought that, owing to the presence of active oxygen, under certain conditions irradiated sterols might play the rôle of catalysts of oxidation processes. Experiments were carried out on oils because of the solubility of sterols in these compounds. Two highly unsaturated oils were chosen, linseed oil and cod-liver oil, and a gravimetric method was employed. A few drops of a one per cent. solution of a sterol in the oil to be studied were added to equal quantities of the oils. Oxygen was passed in and weighings were made every two days for 30 days.

For the oxidation of linseed oil, ergosterol from yeast, irradiated for half-an-hour, was the most active. The oxidation was intensified in the ratio of 2·54: 1. For the oxidation of cod-liver oil, the sterol from cod-liver oil, irradiated for half-an-hour, was most active, the acceleration being in the ratio of 2·98: 1. Ergosterol irradiated for half-an-hour accelerates linseed oil in the proportion of 2·54 to 1, and cod-liver oil in the ratio of 1·60: 1, whereas the sterol of cod-liver oil accelerates cod-liver oil in the ratio of 2·98: 1 and linseed oil in that of 1·64 : 1. Some experiments were carried out in diffused light and others in darkness. The following conclusions are reached:—(1) Sterols are oxidation catalysts for drying oils. (2) They are specific catalysts for the oils from which they are obtained. (3) Irradiation accelerates this action, with a maximum at the end of half-an-hour and a limit at 10 hours of irradiation. (4) This irradiation takes place in air or in an atmosphere of nitrogen, with all the spectrum, or in *X*-rays, without modification of the activating effect. (5) Light is indispensable to this catalysis. Therefore the irradiated sterols appear to be for oils transformers of light energy.

P. H. P.

Organic Analysis.

Partial Iodine Value of Linseed Oil. F. Fritz. (*Chem. Ztg.*, 1930, **54**, 213.)—Direct titration with Wijs' solution dissolved of linseed oils (iodine values 179·1, 181·5 and 183·2) in carbon tetrachloride gave the partial iodine values 116, 116·7 and 118·6, respectively. The end-point, which is difficult to see, is the disappearance of the pale violet colour of the solution of the oil, and is facilitated by suitable lighting arrangements, and by use of comparison solutions and of pale-coloured Wijs' solution. Immediate back-titration of an excess of added Wijs' solution gave unsatisfactory results, iodine values of 123·2, 125·2 and 125 being obtained.

J. G.

Sensitive Reaction for Colophony or Resin Acids. F. Michel. (*Chem. Ztg.*, 1930, **54**, 182–183.)—In the author's modification of the Liebermann-Storch-Morawski reaction a solution of the substance in 3 c.c. of pure chloroform is mixed well with 5 c.c. of sulphuric acid (sp. gr. 1·57). A yellow colour in the acid layer indicates over 3 mgrms. of colophony. Acetic anhydride is then added to the top (chloroform) layer, drop by drop, when in the presence of over 1 mgrm. of colophony a vivid violet is produced, which on violent shaking appears in the sulphuric acid layer as a purple to carmine-red coloration stable for a day. More acetic anhydride should be added till no further colour is produced in the chloroform layer (sp. gr. 1·50). Mineral oils, fats and fatty acids are extracted with cold 70 per cent. (or warm 50 per cent.) alcohol, and the residue after filtration and evaporation to dryness extracted with chloroform and tested. Soaps are decomposed with acid and treated similarly, while volatile substances may be removed by steam-distillation. Paper and wood-pulp are extracted with chloroform directly. The absorption bands of maximum intensity of the colour in acid solution are at γ 580 and 511. If the colour changes to brown the presence of nitrites is indicated.

J. G.

Reaction of Aromatic Aldehydes. M. V. Jonescu. (*Bull. Soc. Chim.*, 1930, **47–48**, 210–214.)—Small quantities of indanedione and of the aromatic aldehyde are dissolved in 1 c.c. of boiling alcohol, and 2 or 3 drops of a dilute alcoholic solution (about 10 per cent.) of piperidine added, and, after warming for 2 to 3 minutes, the mixture is neutralised with glacial acetic acid, cooled, and the coloured crystals of the characteristic arylidene indanedione filtered off and washed with cooled alcohol. It is identified from a consideration of its properties, including colour in the solid state, colour of alcoholic, of acid and of alkaline solutions, and melting point; these data are tabulated for a large number of aldehydes.

D. G. H.

Detection and Determination of Small Amounts of Pyridine. J. W. Kulikow and T. N. Krestowosdwigenskaja. (*Z. anal. Chem.*, 1930, **79**, 452–459.)—The method depends on the production with aniline and cyanogen bromide of a coloured compound of the type *R*.NH.CH:CH.CH:CH.CH:N*R*.HBr. *Iso*-amyl alcohol is shaken with 20 per cent. of 5 per cent. sulphuric acid for an hour, washed neutral with water, distilled, and the fraction obtained at 128 to 132° C. freed from water and redistilled. The product should contain less than 0·025 mgrm. per litre of pyridine, *i.e.* a mixture of 50 c.c. with 1 c.c. of alcoholic cyanogen bromide solution (*vide infra*), and 1 c.c. of a 3 per cent. solution of aniline in *iso*-amyl alcohol should give no colour after 2 hours. Cyanogen bromide is prepared by the gradual addition to 40 c.c. of bromine water of a 10 per cent. solution of potassium cyanide, in the cold, until the colour disappears. The mixture is then shaken with 12 c.c. of *iso*-amyl alcohol and the alcoholic layer separated. For the determination, 20 c.c. of the test-solution are shaken in a stoppered cylinder with 1 c.c. of fresh cyanogen bromide solution, 1 c.c. of a saturated aqueous solution of freshly-distilled aniline added, and the mixture shaken with 10 to 15 c.c. of the pure *iso*-amyl alcohol. The yellow to orange colour may be matched in a colorimeter with that produced by a standard solution of pyridine (b.pt. 114 to 116° C.). For from 0·005 to 0·75 mgrm. of pyridine the maximum error was +0·7 to −1·5 per cent. Solutions containing more than 100 mgrms./litre should be diluted. For micro-work, 1 drop of test solution is mixed with 2 drops of aniline-water and poured on to a disc of filter paper (1·5 cm. in diameter) which is allowed to dry upon the convex side of a watch-glass. It is then placed over an aqueous solution of cyanogen bromide in a crystallising-dish, when a colour permanent for 1 month is produced on the paper and may be matched against discs prepared in a similar fashion from known quantities of pyridine. The sensitiveness is 0·0002 mgrm., but if the presence of alkali is suspected the paper should be exposed for 30 minutes to hydrochloric acid vapours and then to air. J. G.

Inorganic Analysis.

Gasometric Determination of Water (Moisture) by Means of Calcium Hydride. O. Notevarp. (*Z. anal. Chem.*, 1930, **80**, 21–56.)—A detailed and

lengthy account is given of a process and apparatus for determining water in materials containing also other volatile compounds. The process is based on the action of calcium hydride on water, $CaH_2+2H_2O=Ca(OH)_2+2H_2$, the liberated hydrogen being collected over absolute glycol and measured in a Lunge gas volumeter. The paper illustrates the application of the method to, and gives results for, nitroglycerin, nitroglycol, blasting gelatin, nitrotoluene, nitrobenzene, dynamite, ammonium nitrate explosives, mineral oils, coal tar, butter, nitrocellulose explosives, glycol, glycerine, coal, cellulose, and flour. The original should be consulted for working details. W. R. S.

Determination of Copper in Organic Materials. E. Cherbuliez and S. Ansbacher. (*Helv. Chim. Acta*, 1930, **13**, 187–194.)—The organic material is destroyed by oxidation with sulphuric and perchloric acids in the presence of nitric acid (*cf.* Cherbuliez, *id.*, 1929, **12**, 218), the solution diluted so as to contain about 10 per cent. by volume of acid, and a mixture of copper sulphide and sulphur precipitated from the hot solution by means of hydrogen sulphide. The precipitate is filtered off, preferably in a crucible with a porous base, washed, the copper sulphide dissolved in concentrated nitric acid, the solution evaporated to dryness, and an aliquot portion of an aqueous solution of the residue used to obtain an estimate of the amount of copper present. A volume of less than 10 c.c., containing not more than 0·05 mgrm. of copper, is mixed with 3 drops of concentrated ammonia, and the nitroso-chromotropic acid reagent (*vide infra*) added in small quantities. A violet colour similar to that of the permanganate ion is produced at first, and at the end-point this changes to brown. Daylight should be used, and if comparison is made with standards adjusted so as to be on either side of the end-point, an accuracy of titration of 1 per cent. is obtainable. The reagent (1:8 dihydroxy-2-nitroso-3: 6-naphthalene-disulphonic acid, Brenner, *id.*, 1920, **3**, 90) is prepared from a solution of 0·37 grm. of the sodium salt of chromotropic acid in dilute sodium carbonate solution, to which is added 0·5 c.c. of 2 *N* sodium nitrite solution and an excess of acetic acid. After 24 hours the solution is filtered, made just alkaline with sodium hydroxide solution, diluted to 100 c.c., and 34 c.c. of the liquid diluted to 1 litre with water, 50 c.c. of alcohol being added to prevent precipitation). Then 1 c.c. represents 0·01 mgrm. of copper, the exact titre being obtained by titration of a standard solution of copper sulphate containing 0·05 mgrm. of copper per litre. Tap-water distilled from glass apparatus should be used throughout, as distilled water was found to contain copper, and blank tests should be made on the reagents. Less than 0·05 mgrm. of copper may be determined to within 0·0005 mgrm. Amounts of ammonia above that cited obscure the end-point, and salts of mercury, lead, cadmium and tin influence the result to a slight extent when they are present in amounts equal to or greater than that of the copper. When they are in a ten-fold excess over the copper the percentage errors are mercury and lead (+10), cadmium (+6·5), and tin (−2·2).

J. G.

A Reaction of Lead. L. Bey and M. Faillebin. (*Bull. Soc. Chim.*, 1930, **47–48**, 225–226.)—The lead solution is added to 5 c.c. of a solution containing 5 c.c. of ammonia in 100 c.c. water, left for some minutes with occasional shaking, and 5 c.c. of a 5 per cent. solution of resorcinol added, when a blue colour is obtained; in the case of, for example, 0·001 grm. of lead acetate in 19 minutes; and with 0·0003 grm. in 1½ hours. A concentration of 0·003 grm. of lead per litre represents the lower limit of sensitiveness. By this reaction minute quantities of lead as sulphate may be identified in the presence of barium sulphate. A solution containing about 1 part in 1000 of lead sulphate was prepared by pouring a suitable quantity of barium nitrate and lead acetate into dilute sulphuric acid. One grm. of precipitate (0·0001 grm. of lead sulphate) was suspended in 5 c.c. of the ammonia solution for 1 day, after which 5 c.c. of the resorcinol solution were added, and a standard was made at the same time containing 1 grm. of barium sulphate. After 2 hours the supernatant liquid was a distinct blue and the precipitate grey, whilst the standard liquid was greenish. D. G. H.

Determination of Cobalt in Steel. E. Bertrand. (*Bull. Soc. Chim. Belge*, 1929, **38**, 364–371.)—Small quantities of cobalt may be determined colorimetrically by a comparison with a standard series of steels of the same nature as the sample to be tested. The filings (1 grm.) are dissolved in 20 c.c. of strong hydrochloric acid, the solution oxidised with nitric acid, diluted with 20 c.c. of water, precipitated with 30 c.c. of ammonia (strength not given), and filtered through pleated paper. The filtrate is treated with 3·5 c.c. of 30 per cent. tartaric acid, and 5 c.c. of ferricyanide solution (2 grms. per litre), which produces a brownish-red colour; 5 c.c. of 10 per cent. hydrogen peroxide change this to a faint to deep pink. Any blue colour of the ammoniacal solution, caused by nickel or copper, must be discharged by drop-wise addition of cyanide solution. For larger amounts of cobalt the following electrolytic process is used: the filings (2 grms.) are dissolved in 30 c.c. of strong hydrochloric acid by warming in a 500 c.c. flask. The solution is boiled with nitric acid, diluted to 150 c.c., and precipitated with a slight excess of zinc oxide emulsion. It is cooled, made up to volume, and filtered through dry paper. Then 250 c.c. of filtrate are treated with one grm. of zinc oxide and 30 c.c. of saturated bromine water, and boiled for one minute, the cobalt being precipitated. In presence of the soluble zinc salt the separation of cobalt from nickel is stated to be quantitative; any manganese present is also precipitated, with the exception of traces which are oxidised to permanganate in presence of the cobalt salt. The precipitate is collected at once and washed with boiling water, returned to the precipitation vessel, and dissolved in 5 c.c. each of sulphuric and nitric acids, 40 c.c. of water, and a few drops of hydrogen peroxide. The latter is boiled off, and the solution neutralised with ammonia, of which an excess of 25 c.c. is added, together with 0·15 grm. of sodium sulphite. The electrolysis is conducted at 85° C. (±5°) with 0·25 ampère for 1½ hours. If any delay occurs in the deposition, sodium sulphite should be added in doses of 0·05 grm.: the electrolyte should present an orange-yellow, not pink, colour. (*Cf.* Agnew, ANALYST, 1928, **53**, 31.) W. R. S.

Separation and Determination of Nickel and Cobalt Salts. F. G. Germuth. (*Chemist Analyst*, 1930, **19**, 4–10.)—Comparative experiments have been carried out with the four following reagents:—(1) *α-Benzil-dioxime* gives highly accurate results for the gravimetric determination of 5 to 30 mgrms. of nickel in the presence of up to twice this amount of cobalt. Silver, magnesium and zinc do not interfere, but if manganese or chromium occur, the precipitation should take place in the presence of acetic acid or cupric ammonium chloride, respectively, to avoid occlusion by the nickel precipitate. (2) *Dimethyl-glyoxime* (Atack, ANALYST, 1913, **38**, 316) may be used safely for determinations of 20 to 120 mgrms. of nickel in the presence of less than 100 mgrms. of cobalt. Occlusion of chromium is avoided as in *Method* 1. (3) Potassium nitrite (Scott, *Standard Methods of Chemical Analysis*) is not recommended for cobalt determinations on account of the time required and of the difficulties of technique. The method is, however, unaffected by manganese and by 50 per cent. of nickel. (4) *Nitroso-β-naphthol* should be used for small amounts of cobalt (20 to 100 mgrms.) in the presence of relatively large amounts of nickel (50 to 800 mgrms.), but copper, iron, silver, bismuth or chromium interfere with the precipitation. More than 1·5 per cent. of tin is precipitated as a tin-cobalt compound to an extent which is increased if bismuth is present. Details of procedure are not given. J. G.

Determination of Tungsten with Phenylhydrazine. G. Dortreppe. (*Bull. Soc. Chim. Belge*, 1929, **38**, 385–386.)—The alkali tungstate solution (50 c.c., containing about 0·2 grm. of WO_3 and 2 grms. of KCl) is poured into a solution of 1 grm. of phenylhydrazine hydrochloride in 50 c.c. of 8 *N* hydrochloric acid. The white precipitate flocculates immediately and turns greenish. After one hour on the water-bath, the solution is decanted off, the precipitate collected, washed with a one per cent. solution of the phenylhydrazine hydrochloride in 5 per cent. hydrochloric acid, then once with water, and ignited to WO_3. W. R. S.

Determination of Beryllium in Steel. F. Spindeck. (*Chem. Zeit.*, 1930, **54**, 221).—The procedure applies to steels containing no aluminium. The drillings (1 grm.) are dissolved in strong hydrochloric acid, the solution oxidised with nitric acid, and evaporated twice to eliminate silica, filtering after each evaporation. The boiling filtrate (500 to 600 c.c.) is gradually treated with sodium acetate until the basic ferric acetate flocculates, chromium being also precipitated. The bulk is made up to 1000 c.c.; half this volume is filtered and evaporated to 30 c.c. If a very small iron precipitate forms during the concentration, it is filtered off and washed with dilute sodium acetate solution. The filtrate is treated with excess of hydrochloric acid, boiled two minutes, and the beryllium precipitated with ammonia. The precipitate is treated as usual and weighed as BeO. High chromium steel should be dissolved in sulphuric acid, and the chromium oxidised with silver nitrate and ammonium persulphate. The silver is precipitated as chloride, which is filtered off; iron and beryllium are precipitated with ammonia. The well-washed precipitate is dissolved in hydrochloric acid, the solution evaporated to low bulk, diluted, and treated with acetate, etc., as described above. W. R. S.

Iodimetric Determination of Chromate in Presence of Organic Matter. F. Feigl, K. Klanfer and L. Weidenfeld. (*Z. anal. Chem.*, 1930, **80**, 5–12.)—Chromic salt is oxidised in alkaline solution to chromate by hydrogen peroxide or bromine. The destruction of excess oxidant, prior to iodimetric titration, is tedious and rather uncertain in presence of albuminoid matter (*e.g.*, in tannery liquors). Two methods were devised to overcome the interference. (1) The solution, containing 0·02 to 0·03 grm. of chromium as chromic salt, is treated with 20 c.c. of 2 *N* caustic soda solution and 30 c.c. of 3 per cent. hydrogen peroxide. The solution is boiled till yellow, then slowly treated with 5 c.c. of 5 per cent. nickel nitrate solution, care being taken to avoid excessive effervescence; catalytic decomposition of the hydrogen peroxide takes place. When the reaction has abated the liquid is boiled for another 3 minutes, cooled, treated with 2 c.c. of *N* potassium iodide solution, followed by 10 c.c. of strong hydrochloric acid, and titrated with thiosulphate. (2) The same solution is treated with 20 c.c. of 2 *N* caustic potash and 10 c.c. of strong bromine water, and boiled till yellow. It is treated with 3 c.c. of 0·1 *N* potassium thiocyanate solution, and cooled; after addition of 2 c.c. of *N* potassium iodide and 60 c.c. of 2 *N* sulphuric acid, the iodine is titrated with thiosulphate. The thiocyanate reduces the hypobromite to bromide, being itself converted into cyanate. On acidification the chromate reacts normally with the iodide without affecting the excess thiocyanate. W. R. S.

Microchemical.

Micro-determination of Caffeine in Coffee. A. C. Röttinger. (*Mikrochemie Pregl-Festschrift*, 1929, 308–312.)—Caffeine is extracted from coffee powder moistened with ammonia, and the pure caffeine in the raw caffeine extract is determined from the nitrogen content, as obtained by the micro-Kjeldahl method. This is an improvement on the author's previous method (*Z. Unters. Lebensm.*, 1927, **53**, 146), which gives too high values in the analysis of so-called "caffeine-free" coffee. From 10 to 20 grms. of coffee are ground as finely as possible and well mixed, and 5 grms. are weighed in an aluminium boat and placed in the upper part of an apparatus consisting of a 100 c.c. conical flask fitted by means of a ground glass stopper on to a separating funnel above. The coffee is moistened with 5 c.c. of 10 per cent. ammonia, 100 c.c. of chloroform are added to the conical flask, and the two parts of the apparatus are assembled and shaken for 30 minutes. (A Soxhlet apparatus may be used for this extraction if preferred.) The apparatus is then inverted over a pipette fitted with 2 taps and a side tube, and graduated to deliver 20 c.c. The extract liquid is run directly into the pipette through a loose pad of cotton wool. In this way alteration in the concentration of the chloroform extract is avoided. The extract is then transferred to a bulb with two side tubes at right angles; one of these has a ground-in extension containing a wad of cotton wool. For material poor in caffeine a further 20 or 40 c.c. of extract are added to the bulb. The bulb is placed in a water-bath, a few pieces of ignited marble are added, and the chloroform evaporated off by attaching one of the side

tubes to the pump and passing a current of air through it. A small fragment of paraffin wax, and 1 or 2 c.c. of ether are added to the residue, which is gently warmed and then well shaken with a few c.c. of 0·5 per cent. hydrochloric acid. The ether is removed by a current of air, and the paraffin wax sticks to the side of the bulb on cooling; then the liquid is poured through the cotton wool pad in one of the side tubes of the bulb into a separating funnel. The residue is again melted and shaken with a few c.c. of hydrochloric acid, cooled, and the liquid poured into the separating funnel. This is done 4 times in all. The liquid in the separating funnel is then extracted 4 times with a few c.c. of chloroform, and the chloroform fraction filtered through a cotton wool pad each time. For ordinary coffee material the chloroform extracts can be collected directly in the Pregl micro-Kjeldahl tubes, a few pieces of marble added, the chloroform evaporated, and the micro-Kjeldahl determination carried out as in the Pregl method, but with the use of 2 c.c. of concentrated sulphuric acid for the destruction of organic matter. When material poor in caffeine is used the first chloroform extract must be further purified. It is transferred to another bulb apparatus with two side tubes, the chloroform evaporated, and the residue taken up with 10–20 c.c. of water, and for raw coffee 1 c.c., and for roasted coffee 3 c.c. of a 1 per cent. potassium permanganate solution are added, and the mixture allowed to stand 15 minutes in the cold. The excess of permanganate is removed by adding, drop by drop, a solution containing 3 c.c. of 30 per cent. perhydrol and 1 c.c. of glacial acetic acid in 100 c.c. of water. The bulb is then heated for about 15 minutes in a boiling water bath, and the liquid poured through the cotton wool filter into a separating funnel, the bulb being washed out a few times with hot water. The solution in the separating funnel is then extracted with chloroform, the chloroform solutions collected, in the micro-Kjeldahl tubes, and the micro-Kjeldahl determination carried out as above. The accuracy of this method is considerably greater than with the macro method; comparative results by both methods on sets of 3 determinations of the same sample gave the largest difference between analyses on the macro scale 7 per cent.; on the micro scale 1·25 per cent. J. W. B.

Microchemistry of Cystine. M. Wagenaar. (*Pharm. Weekblad*, 1930, **67**, 205–207.)—Cystine ($C_{11}H_{14}N_2O$) has refractive indices α- and β 1·73, 1·64, is a strong base, crystallising in prisms, with melting point 153° C. It is easily soluble in water and alcohol, but almost insoluble in ether, chloroform and benzene. Cystine sublimes in thin plates and needles which tend to form star-shaped crystal aggregates. By precipitation cystine is with difficulty obtained in crystalline form.

Reaction with	Limit of conc. for reaction to occur.	Smallest amount detectable in μ grms.
Mercuric chloride	1 : 300	5
Potassium mercuric iodide	1 : 1000	2
Cadmium iodide	1 : 500	5
Gold chloride	1 : 1000	2
Platinic chloride	1 : 1000	2

J. W. B.

Micro-determination of Silver in Blood and Organs. L. Pincussen and W. Roman. (*Mikrochemie. Pregl.-Festschrift*, 1929, 296–299.)—A titrimetric method is described for the determination of about 0·01 mgrm. of silver in biological material, with an error of 2 per cent. In this method 1–5 c.c. of blood or 1–5 grm. of the material are digested in a porcelain or Jena glass centrifuge tube with 2 c.c. of concentrated nitric acid and 4–5 drops of hydrogen peroxide perhydrol, a few drops of dilute hydrochloric acid are added to ensure the precipitation of the silver. The tubes are carefully heated on a sand-bath, with a small flame, for about an hour. When oxidation is complete the solution, which should be light yellow, is diluted with water and centrifuged for 10 minutes, and the supernatant liquid removed. The precipitate is repeatedly mixed with a few c.c. of water and centrifuged until free from chlorides. The silver is then reduced by adding about 1 c.c. of concentrated ammonia and 10 c.c. of boiling 25 per cent. dextrose solution, which should not be more than 2 days old. The mixture is centrifuged, and metallic silver should then separate and the solution be clear. When more than 1 mgrm. of silver is present the solution may be coloured brown with colloidal silver, in which case 0·5 grm. of solid magnesium sulphate must be added, and the mixture again centrifuged. The clear solution is removed, and the silver finally centrifuged after mixing with water, and then dissolved in 1 c.c. of dilute nitric acid, if necessary by warming. The solution is transferred to a small Erlenmeyer flask, and after the addition of a few granules of iron ammonium alum as indicator, it is titrated against 0·001 *N* ammonium thiocyanate solution, a Pincussen microburette (*Biochem. Z.*, 1927, **186**, 32) being used. Test analyses on a sample of silver-free blood, to which 0·0107 mgrm. of silver had been added, gave titration values of 0·100 and 0·102 c.c. of 0·001 *N* ammonium thiocyanate, and silver found 0·0107 and 0·0109 mgrm. J. W. B.

Use of Isomeric Amino-naphthol-sulphonic Acids for Colorimetric Determination of Phosphate. Béla Vásárhelya. (*Mikrochemie. Pregl-Festschrift*, 1929, 329–337.)—The amino-naphthol-sulphonic acids 1: 8: 4–, 2: 3: 6– and 2: 8: 6–, and the amino-naphthol-disulphonic acids 1: 8: 2: 4–, 1: 8: 3: 6–, 1: 8: 4: 6– and 2: 8: 3: 6– have specific effects on the development of the blue molybdic oxide from the phosphomolybdate complex. Compared with the Fiske-Subbaron 1: 2: 4–sulphonic acid, they show a delayed development of maximum colour, after which some give a considerably deeper colour intensity. The rapidity of colour development depends on the relation of the SO_3H groups to the NH_2 group. Except for the 1, 2, 4-amino-naphtholsulphonic acid, the reaction was impeded by large concentrations of sodium chloride, sodium nitrate, and ammonium sulphate, and by the presence of nitrites, iron and oxalates. A large excess of silicic acid (Si: P=50 : 1) affects the use of the 1, 2, 4-acid, and gives much too high results. J. W. B.

Physical Methods, Apparatus, etc.

The Transfer of Moisture through Fabrics. J. Gregory. (*J. Text. Inst.*, 1930, **21**, T66.)—Transference of moisture through fabrics may be divided into three stages:—(*a*) Between liquid surface and the underside of the fabric; (*b*) through the fabric; (*c*) between the upper surface of the fabric and the free atmosphere in contact with it. The method of testing the rate of transference of moisture is by measuring the rate of escape of water vapour from a shallow glass dish (containing water at 37·5° C., and to the mouth of which one layer of the fabric is fixed) to still air at 20·5° C. and 63 per cent. relative humidity. The time of transfer should not exceed 4 hours, since a longer period would involve an appreciable change in the water level. A number of fabrics were tested of very varying construction, including those for use in the tropics. The greatest rate of transference found was in the case of plain weave (no filling), where the rate was 0·0055 grm. per second per 1000 sq. cm. Weft sateen, duck, cellular woven fabric, and acetate silk gave figures of 0·0049 to 0·0050 grm. The results are not widely different, but considerable differences are revealed when the value for permeability to air (P) is considered. This value is expressed as the number of litres of air passing through 1000 sq. cm. in one second under a pressure difference of 1 mm. of water. In the case of plain weave (no filling), P has a value of 2·2 to 3·5, whereas in weft sateen it is 0·15. R. F. I.

Centrifuge Tube with Removable Cap. A. Friedrich. (*Mikrochemie Pregl-Festschrift*, 1929, 103–105.)—The difficulty of decanting the liquid, after centrifuging, without losing any precipitate, is avoided by using centrifuge tubes with a small removable cap. In this cap the precipitate can be dried, and, if necessary, weighed on the micro-balance. The best form of tube has a volume of 10–15 c.c., larger sizes being difficult to make, as the cap must be placed centrally under the tube. The tube is ground to fit not too tightly inside the glass cap, and the two are cemented together with Krönig's glass cement, which is loosened by placing in warm water, and cleaned off with benzene. While centrifuging, the tubes should rest on rubber mats. (Tubes obtainable from Paul Haack, Vienna.) J. W. B.

Reviews.

APPLIED INORGANIC ANALYSIS. WITH SPECIAL REFERENCE TO THE ANALYSIS OF METALS, MINERALS, AND ROCKS. Dr. W. F. HILLEBRAND and Dr. G. E. F. LUNDELL. Pp. xix+929. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1929. Price 42s. 6d. net.

It can hardly be disputed that the massive work under review is destined to be one of the most important reference books on inorganic analysis in the English

language. Probably not since Rose's time has an analytical treatise such as this appeared, in which all elements are accorded equal treatment; a welcome sign that the arbitrary and out-of-date distinction between "common" and "rare" elements is beginning to disappear. Thus, with the exception of the platinum metals chapter, the longest chapter in Part II is that on tantalum and niobium. The book is no ordinary compilation; it is severely critical, even, as I think, hypercritical in some cases. Numerous test analyses, given in footnotes, have been made to prove or confirm the reliability of methods described.

The subject-matter, in five Parts, deals with (1) General Considerations, (2) the Determination of Elements, (3) Silicate Rock Analysis, (4) Carbonate Rock Analysis, and (5) Glass and Bauxite, distributed over 160, 484, 175, 31, and 21 pages respectively. Tables and Index occupy 58 pages.

Parts III and IV reproduce the late senior author's classic treatise on rock analysis, previously published in the form of bulletins of the U.S. Geological Survey. A review of that part of the book is hardly necessary; all those familiar with petrology know that the name of Hillebrand will remain linked with the analysis of silicate and carbonate rocks.

In Part I are recorded, as "Common Operations," the most important precipitation reactions common to several elements (group reactions) and the analysis of group precipitates, as well as general gravimetric and volumetric technique; there are 20 pages of excellent directions for the standardisation of volumetric solutions. This part of the book is a mine of reliable information.

The determination of all the individual elements, and their separation from associated elements are compressed within the 484 pages comprising Part II. Such an undertaking requires husbanding of space, only a restricted choice of methods being offered. However, those that are described are recorded, whenever possible, in a standardised form, calculated to secure the highest possible degree of accuracy. This part, like the preceding, makes the book an indispensable work of reference for general inorganic analysis.

Many more or less familiar methods have not been included, e.g. Eschka's process for the assay of mercury ores, the bromate method for antimony, the volumetric determination of selenium, tellurium, and thallium. The use of the most tractable cobalt precipitate—cobalt ammonium phosphate—for dealing with large quantities of the metal has not been mentioned. It may not answer the authors' requirements for extreme accuracy, but, if so, one wonders why reference is made to a method based on precipitation by phenylthiohydantoic acid (p. 323), a reagent which causes "partial precipitation of iron and nickel."

A number of methods have been dismissed with a didactic statement of disapproval. Thus, the determination of bismuth as phosphate is placed on a par with those as sulphide, and as metal after cyanide fusion: "none of these should be considered in accurate analyses" (p. 192). No description of any rejected method is, of course, given. Again, potassium iodide is "unsuited for quantitative

work" on selenium (p. 260); and beryllium "can not be precipitated as the phosphate and weighed as the pyrophosphate" (p. 407). In the three cases cited, these views are contradicted by the results of Prof. Moser's investigations.

In other cases, it may be questioned whether the particular method described has not been given at the expense of a better or more convenient procedure. Two examples may be noticed: (1) Parsons and Barnes's bicarbonate process for the separation of beryllium from aluminium "is quite satisfactory, although some beryllium is always carried down with the aluminium" (p. 405). Moser and Niessner's tannin method (ANALYST, 1928, **53**, 401) deserves at least to be placed alongside the older process. (2) Only Mosander's chlorine method for the separation of ceria from other rare earths is given, and commented upon as follows: (p. 438) the separation is "fairly good." . . . "Repeat the whole operation 5 to 10 times. Entire freedom from the other earths can never be obtained." One wonders why Brinton and James's bromate-iodate method has not been included.

Since the appearance of this book, Smith and Ross's butyl alcohol and ethyl acetate method for the separation of the alkalis (p. 523) has been adversely criticised by Moser and Schutt (ANALYST, 1929, **54**, 370), who consider Winkler's isobutyl alcohol process superior to all others. During the past twelve months, much additional information on the analytical chemistry of gallium and indium, by Moser and his co-workers, has become available (ANALYST, 1929, **54**, 64, 367; 1930, **55**, 218).

The separation of manganese from nickel and cobalt is one of the least satisfactory propositions in the analysis of the common metals. Here the book has no helpful advice to offer: the precipitation of nickel and cobalt sulphides from acetate solution "is not entirely satisfactory as the precipitation is rarely complete" (p. 314). I venture once more to call attention to the xanthate method (ANALYST, 1919, **44**, 276), as I believe it to be worth rescuing from threatened oblivion.

The treatment of a solution with hydrogen sulphide previous to determination of sulphur as barium sulphate involves a risk which I would not willingly take. The procedure is recommended, *inter alia* for the reduction of ferric chloride (p. 574); yet Curtman and Frankel (*J. Amer. Chem. Soc.*, 1911, **23**, 724) have found that appreciable amounts of sulphuric acid were formed by the oxidising action of the ferric salt.

A few inaccuracies have managed to find their way into this otherwise painstakingly accurate compilation. The mineral stannite has been given the formula SnS_2 (p. 233). In p. 205 we read that "the separation of mercury from cadmium is based on the insolubility of the sulphide of the former in nitric acid (p. 171)"; reference to that page, however, discloses that this "separation fails if the sulphide [of mercury] was thrown down in a solution containing copper, cadmium, or zinc." A wrong description of Dittrich and Freund's salicylate method (p. 455, line 11) is contradicted by the summary given in p. 84: the neutralised solution of the nitrates is *not* boiled, and it should be dropped slowly *into* the boiling salicylate solution, not *vice versa*.

The chapter on the platinum metals and gold is from the pen of Dr. E. Wichers, also of the Bureau of Standards. It contains a great deal of useful and reliable information alongside other data conveyed in cautious or non-committal terms; the text abounds with expressions such as: "appear to"; "seem to"; "it is better to"; "usually best to"; "it is believed that"; "supposedly"; "presumably"; etc.

Speaking as a specialist in the analytical chemistry of the platinum metals, I am bound to express the opinion that an atmosphere of something akin to unreality pervades this chapter; in any case, it can hardly be termed "Applied" Analysis. It is difficult to see how these more or less detached considerations on the decomposition of certain materials, on method of separation, and on the determination of the individual metals, will contribute materially towards the solution of the complex problems encountered in actual practice, which cannot as a rule be openly discussed by those best qualified to do so. It is an easy matter to indulge in destructive criticism of the ammonium chloride method for the analysis of platiniferous materials, which may be "justified by the demands of commercial work for a rapid method of approximate accuracy" leading to accurate determinations "only by accidental compensation of large errors" (p. 284). It is not altogether on determinations of that kind that the transactions of the platinum trade are settled. The time has not yet come for the rejection of ammonium chloride as an important reagent in platinum-metals analysis. Ammonia as a precipitant for alumina in rock analysis is by no means an ideal reagent, yet, *faute de mieux*, it has been made to serve the ends of the petrologist. In the same way, ammonium chloride in practised hands is a most serviceable—possibly indispensable—reagent in precious-metal work. Needless to say, the ammonium chloride precipitate is analysed or re-treated, somewhat like the ammonia precipitate in rock analysis.

So far as I can gather, no alternative to the ammonium chloride method is given, unless the following indications supply a clue: "Hydrogen sulphide affords an excellent means of separation from all except those metals which are likewise precipitated from acid solution by this reagent" (p. 275). "When the latter are present recourse may be had to various more or less specific methods of removing them" (p. 278). These are dealt with in 17 lines of print. When it comes to the separation of the precious metals from one another, it is "assumed that base metals are absent" (p. 278). As to these separation methods, I am certainly not in favour of compilation pure and simple; but I think even compilation is better than the following statement: "the relatively infrequent need for the quantitative determination of ruthenium and osmium is probably responsible for the lack of sufficient knowledge of the separation of these elements from the remaining platinum metals and from each other" (p. 281). As a matter of fact, the separation of rhodium, iridium, and platinum is a much more difficult problem than that of ruthenium and osmium. An unkind critic might say that, strictly speaking, the need for almost half the number of separations given in the book is "relatively infrequent."

The author evidently favours the use of hydrogen sulphide as a precipitant for rhodium and iridium, a procedure which—more particularly in the case of iridium—is too tedious and uncertain for practical work on account of the difficulty of achieving complete precipitation; but, strangely enough, he does not advocate it for ruthenium, for which it has proved to be efficient and convenient. What is given for the determination of ruthenium is a new method based on hydrolytic precipitation of the chloride solution by sodium bicarbonate. The ignition is complicated by the tendency of the precipitate to deflagrate, the operator being even advised to protect himself against a possible explosion (p. 288). The practical chemist will think twice before adopting a process at the end of which the product of several days' hard work is likely to go up in smoke, especially as the determination by the existing methods presents no difficulties or risks whatever. Nor is he willing to invite trouble by forsaking the well-tried gravimetric process for a volumetric method (p. 288) for the "approximate" determination of ruthenium.

The misprints counted in Parts I and II number 48, nearly all obvious printer's slips. A curiously-worded sentence, the sense of which is rather obscure, occurs in p. 590 (lines 16 to 19).

Judged as a whole, the book consists of two distinct sections of widely different character. Parts III to V are exhaustive monographs for laboratory use, minutely describing the complete analysis of a few specified materials; whilst Parts I and II are more in the nature of a work of reference giving all the necessary information for analytical operations, separations, and determinations, but no comprehensive schemes for complete ore or metal analysis or for combining determinations.

The criticisms recorded above are in nowise intended to belittle the value of the book. On the contrary, if I have been critical, it was in the hope of contributing a few suggestions of constructive value, however small, to a remarkable work.

W. R. SCHOELLER.

MONOGRAPHS ON BIOCHEMISTRY. BACTERIAL METABOLISM. By MARJORY STEPHENSON. Pp. 320. London: Longmans, Green & Co. Price 18s.

Miss Stephenson's book is a valuable addition to the well-known series of biochemical monographs which have appeared from time to time under the co-editorship of Professor Plimmer and Sir F. G. Hopkins. While the metabolism of the higher plants and animals has for many years drawn to itself the attention of scientific workers, the metabolism of bacteria has only recently received intensive study from the biochemical standpoint. Much of this work has been carried out by the author and her colleagues in the Sir William Dunn Institute of Biochemistry at Cambridge, and it is appropriate, therefore, that the results of a large amount of brilliant and pioneer work should be gathered together by a worker from this laboratory.

The recent advances which have been made in the study of bacterial metabolism have depended largely on the use of synthetic media and on the careful

analysis of the chemical composition of both media and organisms under conditions of growth, activity, rest, etc. Much of the success in the study of intermediate metabolism depends on recognising intermediate products. As the author herself states, "it is safe to say that it is the highly reactive and fugitive products which the cell uses for building up its own materials, and it is for this reason that the fermentation chemist seldom catches sight of the biologically important products of fermentation. It is only by interfering with the normal course, as is done by Neuberg and others, by the use of fixing agents for special products, or by altering the relative rates of production and removal, that the presence of the reactive biologically important products can be demonstrated." As an example of the detection of intermediate products may be cited Raistrick's isolation of urocanic acid from the bacterial decomposition of histidine, a type of change (from amino acid to unsaturated acid) which may prove to be the necessary first step in the bacterial attack on amino acids in general.

Although the author has given a full account of the work of the Cambridge school, the book is by no means exclusively devoted to this purpose. On the contrary, the width of the literature cited and the lucid exposition of the work of Pasteur, Winogradsky and others is evidence that the reader is obtaining a fair and well-balanced review over a wide field of work. The account of the nitrifying bacteria and the autotrophic bacteria makes fascinating reading both from the chemical and biological point of view. Miss Stephenson suggests that "Perhaps bacteria may tentatively be regarded as biochemical experimenters . . . No large animal or plant, for example, could hope to survive if obliged to depend solely on the oxidation of ammonia or sulphur for its energy. . . . The autotrophic bacteria lead a hard and precarious existence, due to the adoption of a type of metabolism ill adapted to life on this planet, and only possible to organisms whose demands are small."

Miss Stephenson's style makes for easy reading, and her book will be of value not only to bacteriologists but to all chemists who are interested in the possible cycles of chemical change that can and do occur under the action of living organisms.

The publishers have done their work well, and the volume is remarkably free from misprints.

D. JORDAN LLOYD.

ELEMENTARY QUANTITATIVE ANALYSIS. By C. J. ENGELDER, Ph.D. Pp. xii+254 with 8 illustrations. London: Chapman & Hall. 1929. Price 13s. 6d.

This volume is intended for the use of elementary students who have gained some knowledge of theoretical chemistry and qualitative analysis and are commencing quantitative work. In the past the sudden transition experienced by the budding analyst on taking up quantitative analysis has often been a well-remembered milestone in his career; for the change in technique, principles and calculations not infrequently conveys the impression that there is little in common between the two branches of chemistry. For this reason the author has wisely

emphasised the close connection that really exists between the two, and throughout the text this co-ordination is evident.

In Part I the scope, theoretical basis, precision and calculations of quantitative analysis are dealt with, whilst Part II provides instruction in the theory and technique of gravimetric precipitation methods, including the application of the solubility product principle and ionic equilibrium calculations, representative methods in detail for the estimation of sulphates, the halogens, oxalates and phosphates, the electrochemical estimation of copper, and gravimetric evolution methods for the determination of silicates and carbonates. The remainder of the volume contains descriptions of volumetric methods in which neutralisation, oxidation and reduction are involved, and the final pages bear an appendix giving lists of reagents and apparatus required and the usual tables of specific gravities, atomic weights, logarithms, etc. The author has made a careful selection of methods graded in difficulty and suitable to the needs of the student and has endeavoured to impress upon the mind of the latter the value of precision by limiting the number of methods and dealing with each thoroughly. As an instance of this the worker is recommended to carry out three separate gravimetric estimations on the same sample simultaneously, a procedure which would be advantageous to all beginners, besides saving considerable time in the long run. The subject-matter is sound, lucid, and exceedingly well adapted to its purpose; and, although emanating from an American source, there is but little evidence of this in the phrasing or spelling. The care with which the proofs have been read is reflected in the unusual freedom from errors throughout, but "pyrophyosphate" has crept in on p. 95, and a small "n" in the symbol for sodium occurs in a graphic formula on p. 157. These minor defects, together with the omission of the word "concentration" after "hydrogen ion," on p. 149, appear to constitute the only defects in the entire volume.

Such a work as this is of considerable value, and well worthy of attention by all engaged in the teaching of elementary chemistry; for, apart from the excellence of the subject-matter, the text is legible, the general style and binding of the volume are admirable, and the whole production is exceedingly good value for the price charged.

T. J. WARD.

DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. Vol. I, ABELMOSCO TO CUSCUTA. Vol. II, DAMIANA TO MUSSENA. By Professor G. VITTORIO VILLAVECCHIA AND OTHERS. Fifth edition, revised and enlarged. Milan: Ulrico Hoepli. 1929–1930. Price 60 lire each volume.

The appearance of this new edition six years after the preceding one (reviewed in THE ANALYST for December, 1923), now sold out, is sufficient evidence of the popularity of the work. The general form remains unchanged, but certain small improvements have been introduced. The higher quality of the paper and the discontinuance of a number of the abbreviations formerly employed deserve special mention.

The subject-matter has been brought up to date on both the technical and the statistical sides, and a large proportion of the total number of articles has been very considerably enlarged. This is the case, for example, with the sections dealing with mineral waters and with the various alcohols, and the completeness of treatment may be judged from the fact that the article on ethyl alcohol, including denatured alcohol, now extends to 40 columns (20 pages).

In addition, a number of substances are either introduced as new subjects or given separate headings, these including acetonitrile, maleic acid, malonic acid, cumic alcohol, algae, anti-knock compounds, arsenobenzenes, petroleum spirit, and carbazole. In these various ways the first volume of the fourth edition has undergone expansion from 872 columns to 1223 in the present edition.

As a rule, the English equivalents are given correctly, and a number of misprints and slight errors in spelling have now been rectified. There still remains, however, an appreciable number of such mistakes. Japan lac is given as Japanese lake, but perhaps the most curious expressions noticed are "cryptogam's antidotes" (fungicides) and "succedaneous of butter" (butter substitutes).

These slight blemishes do not detract from the value of the book, which will be found of use to British chemists. This is particularly the case with such sections of the two volumes as deal with Italian products, and with those treating of sulphur, olive oil, etc., which will appear in the two volumes yet to be published. The alphabetical index will add greatly to the usefulness of the dictionary.

Increase in magnitude has necessitated a corresponding increase in price from 35 to 60 lire per volume, but, in comparison with English, German, and American scientific publications, the book is still remarkably cheap.

T. H. POPE.

MIKROCHEMIE. PREGL-FESTSCHRIFT. Pp. xii+340, with 60 illustrations and 1 photograph. Vienna and Leipzig: Emil Haim & Co. 1929. Price R.M. 25.

This volume is a special issue of *Mikrochemie* to celebrate the sixtieth birthday of Professor Pregl, the father of organic micro-analysis, and the winner of the Nobel prize. It contains thirty-eight original papers, of which nineteen come from the three Austrian Universities, Vienna, Graz and Innsbrück, and the rest from authors in Germany, Switzerland, Norway, Sweden, France, Czechoslovakia, and the United States. The papers cover the whole range of micro-chemistry, physical, organic, inorganic, and biological, both qualitative and quantitative. Abstracts of most of the papers are appearing in THE ANALYST.

J. W. BROWN.

Erratum.

Preliminary Studies in the Bacteriology of Wheat and Flour: In the plate facing p. 262 the description of Fig. 2 should read "Film preparation of 'ropy' bread," as in the text, p. 261.