

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, May 2nd, the President, Mr. John Evans, F.I.C., being in the chair.

Certificates were read in favour of John Ferguson Brown, B.Sc., A.I.C., Carl Emil Resch, B.Sc., Wilfred Smith, B.Sc., A.I.C., and Sidney George Edward Stevens, B.Sc., A.I.C.

The following were elected members of the Society:—Frederick Frank Beach, M.A., B.Sc., F.I.C., Thomas Gifford Elliot, F.I.C., Frederick John Flowerdew, B.Sc., A.I.C., M.P.S., John Arthur Heald, M.C., B.Sc., F.I.C., Francis Edwin Needs, F.I.C., and Derrick John Saxby, B.Sc., A.I.C.

The following papers were read and discussed:—"The Determination of Free Silica in Coal Measure Rocks," by A. Shaw, B.Sc.; "A New Apparatus for Determining the Temperature of Crystallisation of Cocoa Butter," by S. A. Ashmore, B.Sc., A.I.C.; "The Determination of Small Quantities of Germanium in the Presence of Arsenic," by S. A. Coase, B.Sc.; and "The Saturated Fatty Acids of Chrysalis Oil," by S. Ueno and H. Ikuta.

Obituary

WILLIAM ELLAND WOOLCOTT

By the death of William Elland Woolcott, on April 14th, the Society has lost one who will be much missed, especially by his fellow consultants.

Mr. Woolcott was a partner in the firm of A. Norman Tate & Co., with whom he had been associated for forty-six years, practically all his adult life, and was well known for his work on oils and fats. He served on the Committee appointed by the Ministry of Food, under the Chairmanship of the late Otto Hehner, to report on Standard Methods of Analysis of Seeds, Nuts and Kernels, Fats and Oils and Fatty Residues, which completed its labours in 1919 (see ANALYST, 1920, 45, 278).

He joined our Society in 1921, and was elected a Fellow of the Institute of Chemistry in 1922. Of a singularly modest and retiring disposition, he was seldom heard at meetings of the chemical societies which he attended, but his confrères knew him as one who was ever ready to assist them with his knowledge and advice on any subject of which he was a master.

A few years ago a serious illness affected his health, but he continued working in the laboratory until some days before his death at the age of 65. His nervous temperament caused him, of late years, to worry over the future welfare of his colleagues and assistants, and the time of business depression left its mark upon him. There is little doubt that this incessant anxiety weakened his powers of resistance, and thereby hastened his end.

The funeral, which took place at Bebington Cemetery, was attended by Mr. W. Roscoe Hardwick and the writer.

F. ROBERTSON DODD

The Determination of Small Quantities of Fluorides in Water

BY GUY BARR, B.A., D.Sc., AND A. L. THOROGOOD, B.Sc.

(Read at the Meeting, April 4, 1934)

WE have made a short study of the application of the zirconium-alizarin reagent of de Boer (*Rec. Trav. Chim. Pays-Bas*, 1925, **44**, 1071; *Chem. Weekbl.*, 1924, **21**, 404) to the colorimetric determination of small quantities of fluorides. After the work had been completed a paper by Elvove (*U.S. Public Health Reports*, 1933, **48**, 1219) appeared, describing a procedure nearly identical with that which we had evolved; many of the observations given below are, however, not to be found in his brief note. References to the literature of the subject will be found in Elvove's paper.

The stock solutions used in making the reagent were: (a) 3.53 grms. of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) dissolved in 100 ml. of distilled water (1 ml. contained 10 mgrms. of zirconium); (b) 1 gm. of sodium alizarin monosulphonate dissolved in 100 ml. of water and filtered.

To determine the optimum proportions in which solutions (a) and (b) should be mixed, a series of mixtures was made containing a fixed volume of (b) and differing volumes of (a). It was found that when the volume of (a) was less than one-fourth that of (b) the solution was dark yellow; with higher proportions of (a) the reagent was of a reddish-violet colour. On standing for 24 hours a reddish precipitate was formed in the mixed solutions unless the proportion of (a) to (b) exceeded 1.2 to 1. As a reagent for determining traces of fluorine in water, 3 ml. of (a) were mixed with 1 ml. of (b) and diluted to 200 ml. with distilled water. One ml. of this reagent gave with 50 ml. of water a faint pink colour, which was discharged by small quantities of fluorides.

Since de Boer stated that the sensitivity of the fluoride reaction was increased by the addition of hydrochloric acid, experiments were made to determine the optimum concentration of acid. Additions of more than 5 per cent. of concentrated (10*N*) hydrochloric acid to the test-water in the presence of the diluted reagent reduced the colour considerably, even in the absence of fluoride. Reduction of the amount below 5 per cent. made the fluoride reaction very slow.

It was not possible to include the desired amount of hydrochloric acid in the reagent by diluting the mixture of (a) and (b) with acid instead of with water, since this mixture gave a reddish precipitate on standing for 24 hours. In the absence of acid the diluted reagent remained clear for at least a month.

Thompson and Taylor (*ANALYST*, 1933, 58, Abst., 369) and Casares and Casares (*Anal. Fís. Quím.*, 1930, 28, 1159; *Chem. Abstr.*, 1931, 25, 550) used an acid of approximately 2.5 per cent. concentration. Thompson and Taylor increased the speed of reaction by heating, whilst Elvove, who used approximately the same acid concentration as we have done, allowed the test-waters to stand overnight before matching. By using the procedure outlined below it was found possible to secure accurate matching after the solutions had stood for ten minutes only.

To test the sensitivity at low fluoride concentrations, six sodium fluoride solutions were prepared so as to contain from 0 to 1 part of fluorine per million in distilled water. Fifty ml. of each solution were transferred to a Nessler cylinder, 2.5 ml. of concentrated hydrochloric acid (10 *N*) and 1 ml. of the reagent were added, and the mixture was allowed to stand for ten minutes. It was possible to arrange the cylinders in the order of their fluorine-content, the colour varying from pink with no fluorine to brownish-yellow with one part of fluorine per million.

In estimating the fluorine-content of a sample of water it was necessary to ascertain the order of the concentration before proceeding to a precise determination.

This was done by matching the test-sample, by the procedure described above, against a series of standards containing, say, 1, 2, 4, 6 and 8 parts of fluorine per million. If the colour of the test-sample faded at a rate between that of standards 4 and 6, a further series was prepared, sub-dividing the range between these two standards; the process was continued until a perfect match was obtained. For concentrations higher than 2 parts per million the pink colour obtained with 2 ml. of reagent changed to yellow with an inconvenient rapidity. It was necessary, therefore, in the definitive comparison, to use a larger volume, such that a very faint tinge of pink remained in the sample and in one of the standards after ten minutes; thus, for a fluorine-content of 5 parts per million, the volume of reagent was increased to 2 ml. It was found possible to determine the fluorine-content of a sample of potable water containing 5 parts of fluorine per million with an accuracy of 0.1 part per million. Such an accuracy cannot be obtained by Elvove's method, which is essentially similar to that used by us for the preliminary examination, although he suggests, in a footnote, that the proportion of reagent should be adjusted in the manner which we have found to be essential for rapidity and precision.

Concentrations of potassium, sodium and magnesium, exceeding those occurring in potable waters, were not found to affect the fluorine estimation. Since

indications were obtained that the presence of unusual proportions of calcium, iron and sulphates interferes with the determination, it may be necessary, in some cases, to make the final colour comparisons with synthetic solutions having a composition similar to that of the water under examination. Thompson and Taylor have shown that, in determining the fluoride concentration in sea water, considerable discrepancies may arise unless the comparisons are made with waters of equal chlorine-content.

SUMMARY OF METHOD.—To 50 ml. of the water, contained in a Nessler glass, add 2.5 ml. concentrated HCl; mix, and then add such a quantity of the following reagent that a very faint pink tinge remains after standing for 10 minutes. The reagent is made by mixing 3 ml. of a zirconium solution (3.53 grms. $ZnOCl_2 \cdot 8H_2O$ per 100 ml. of water) with 1 ml. of a 1 per cent. solution of sodium alizarin mono-sulphonate in water, and diluting to 200 ml.; for fluorine-contents below 1 part per million, 2 ml. of the reagent give a sufficiently intense pink colour, whilst for 5 parts of fluorine per million 4 ml. will be required, and will yield an orange colour. The colour produced must be matched against that given by standards containing known concentrations of fluorine (as sodium fluoride) treated similarly and at the same time. When the order of concentration is unknown, it is convenient to make a preliminary estimate from the *rate* of disappearance of the pink colour, using 4 ml. of reagent with standards containing 1, 2, 4, and 8 parts of fluorine per million.

This investigation was undertaken, at the request of Mr. N. J. Ainsworth, to obtain a method suitable for the routine examination of drinking waters in connection with studies on dental defects due to fluorides. The cost has been defrayed by him, and we desire to thank him for permission to publish the details.

THE NATIONAL PHYSICAL LABORATORY
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The Clinical Significance of Traces of Fluorides in Water

BY N. J. AINSWORTH, M.C., M.R.C.S., L.R.C.P.

(Read at the Meeting, April 4, 1934)

It has been recognised for some years that excess of fluorides in the diet of animals will produce changes in metabolism which manifest themselves in various parts of the organism.

This pathological condition is termed "fluorosis," and the organs chiefly affected are the bones. Schultz and Lamb,⁶ in 1925, were the first to report on experimental fluorosis. It had not, at that date, been recognised as occurring naturally.

McCollum and his co-workers,⁵ later in the same year, published an account of more extensive experiments on albino rats fed on a diet containing 226 parts of sodium fluoride per million. The changes reported affected not only the quality

but also the growth of the bones, which, in general, seemed under-developed and of a more porous nature. The teeth were dull and opaque, and the normal yellow pigmentation of the front of the incisors was absent. The upper incisors also were so altered in shape that they failed to meet and to be ground away by the lower incisors; they consequently, grew in a circle until they penetrated the skull.

It was not for several years that the condition of the teeth of animals so fed was associated with the endemic disease or dystrophy called by Dr. Black,¹ in 1915, "mottled teeth" from their patchy white appearance; it was left to two chemists, Petrey and Churchill⁷, in 1930, to demonstrate that the water supply in all affected areas in U.S.A. contained over two parts per million of fluorine, and the connection between this fact and the mottling was proved experimentally in the following year by Smith and Lantz⁴, working independently.

A far severer condition is found in North Africa—termed by the French workers "le Darmous." In this the bones and general health, as well as the teeth, are affected, and the condition is sometimes fatal. These cases, I believe, occur in areas where the water flows over certain phosphatic strata—these natural phosphates are contaminated with fluorides.

Velu⁸ carried out experiments on rats, to whose diet were added $1\frac{1}{2}$ to 3 parts per cent. (40 to 80 parts per million of fluorine) of natural phosphate (Moroccan and Algerian phosphates).

The results were much more severe than those recorded by McCollum, and included various forms of paralysis, delayed growth, suppression of the sex cycle, death of offspring, goitre, atrophy of the bone marrow and loss of appetite, as well as the usual alterations in the teeth.

Velu produced similar symptoms by feeding rats on calcium fluoride which, I understand, is almost insoluble, whereas McCollum and most other workers used soluble salts, such as sodium fluoride.

So much for the damage produced by abnormal amounts of fluorides in the diet. There is one other point of some interest. Is fluorine, which is found in all bones, particularly teeth, an indispensable element in the diet?

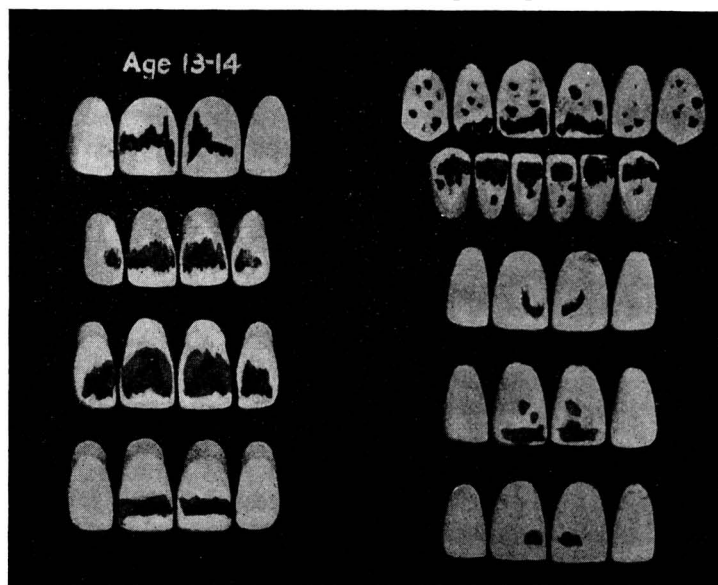
Last year, McCollum and Sharpless⁹ carried out feeding experiments to answer this question, and found that no disadvantage was suffered by rats whose diet contained practically no fluorine; teeth and bones were normal, growth and reproduction unaffected. The interesting point is that in these animals no fluorine could be detected in the teeth.

It, therefore, appears that fluorine, either in food or in the body, is a mere contamination, and is not necessary to life or health, but that small amounts are tolerated, whilst large amounts are definitely harmful.

My interest in this question of the fluorine contamination of water is mainly clinical. I first noticed the dental condition known as "mottled teeth," when a student, in a young patient from Maldon, Essex. Later I had the opportunity of examining a large number of Maldon school children, when it became clear that the condition was identical with that described by Black and Mackay,¹ in 1916, as occurring in many districts of the United States of America between the Mississippi and the Rockies, notably in Arizona (*cf.* Dean²). After the discovery, in 1930, that the water-supply of these districts contained fluorine, I re-investigated the Maldon

conditions, and obtained various samples of the local drinking waters, together with additional photographs³.

The analyses made by Dr. Barr by the procedure he has described showed that the water of unaffected areas was free from fluorine, whereas that from the affected areas contained between 4.5 and 5.5 parts per million.



Teeth of 8 children affected with fluorosis.
Left-hand column: ages 13-14. Right-hand column: ages 12 to 13.
[Reproduced from a drawing, by permission of *The British Dental Journal* (1933, 55, 233).]

A very high proportion (about 90 per cent.) of the children born and bred in these areas were affected, the essential condition being that they should be drinking the water during the years when the teeth were being formed. Once the teeth were through the gums the condition could not be influenced one way or another.

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DISCUSSION

The PRESIDENT said that he was sure all were grateful to the authors for bringing such important papers before them. He asked what was the normal amount of fluorides they had found in ordinary drinking waters, and what variations had been recorded.

Dr. G. MONIER-WILLIAMS said that the authors of the papers were to be congratulated on this piece of work. This was the first time that the connection between fluorine and mottled teeth had been established in this country. It provided one more instance of the great effect on metabolism which might be exerted by minute amounts of certain substances. The effect of fluorine on bone formation had been known for many years. In Maercker's book on the manufacture of alcohol reference was made to the feeding of cattle on distillery residues containing fluorides used as yeast antiseptics. The bones of the cattle were found to be seriously affected.

This matter was of great interest to analysts, in view of the fact that fluorides were seriously advocated some time ago as preservatives. Preparations containing fluorides were openly sold as butter preservatives, and it was claimed that sodium silicofluoride was absolutely non-toxic. Fluorides might also occur in phosphate baking powders and flour improvers made from rock phosphate. Obviously, the presence of more than the merest traces of fluorine was highly undesirable.

Another point of interest was the proposal that silicofluorides should be used as insecticides in agriculture. In France, barium silicofluoride was used against the Colorado beetle, and it was suggested that it should be used on potato crops in this country. If confined to the potato haulm, it might not be objectionable, but the case would be different if it were used on the edible parts of crops.

It was curious that there should be fluorine in the Maldon water. One would have expected it to occur in parts of Derbyshire, but not in water from the London clay. What was the mode of action of fluorine on teeth? Did it remove calcium or did it interfere in any other way with calcium-phosphorus metabolism? Statements in the literature as to the fluorine-content of bones and of sound and unsound teeth were very contradictory.

Mr. D. M. FREELAND, referring to Dr. Monier-Williams' remark regarding insecticides, said that a short time ago he was asked to examine an insecticide, and it contained roughly 50 per cent. of *Dalmatian* flowers and 50 per cent. of sodium fluoride. The manufacturers stated that it would not harm animals. He could understand that they would not wish to eat it, but if it were to get on to any food it would certainly have bad effects. Undoubtedly sodium fluoride should not be put about indiscriminately in houses or factories.

Mr. F. W. F. ARNAUD said that he had known of the use of sodium fluoride in fly poisons for many years. He asked if fluorine had been determined in ordinary drinking water apart from that in the Maldon area?

Mr. A. L. BACHARACH suggested that, in a district where the water contained fluorine, all the produce in the locality might be similarly contaminated, so that the mottled teeth and other pathological conditions might not be due solely to the fluorine in the water. An examination of the fluorine-content of the produce grown and consumed in the district might be desirable to elucidate this matter. It was perhaps vain to speculate at this stage, but one could not help wondering if the ingested fluorine "locked up" some of the available calcium, much as beryllium presumably locked up phosphorus in experimental "beryllium rickets."

Mr. C. E. SAGE asked whether any of the effects described had been noticed among workers using hydrofluoric acid. He had never come across such mottled teeth among men using the acid. Maldon was one of the few places where salt

was produced from sea-water. Was the effect on teeth peculiar to Maldon because of the use of such salt, or, had it been noticed where the salt was prepared from brine pumped in Cheshire or Worcestershire? He also asked if the method was applicable to food.

Mr. W. J. A. BUTTERFIELD remarked, apropos of the Maldon water, that he believed it was a fact that most of the water supplies in Essex contained a comparatively large proportion of chlorine. Was the chlorine in Maldon water in anything like the same ratio to the fluorine as it was in sea-water? He asked this because chlorine extended in relatively high proportions to chalk water from deep artesian wells in Central London. One found these wells, which were sunk by owners of big blocks, to contain organically unimpeachable chalk water, with 16 to 20 parts per 100,000 of chlorine. This was undoubtedly due to very slow infiltration of sea-water from the bed of the river, where the sea-water lay almost undisturbed by the ebb and flow of the tide. Fresh water passed down and sea-water passed up the river, but on the bed there was very little change with the tidal conditions, and he thought it possible that the chlorine-content of the waters in Essex was due to that slow infiltration of sea-water from the coast and tidal rivers.

Dr. J. GRANT asked if the authors had tried the bleaching effects of fluorides on the colour produced by titanium salts and hydrogen peroxide. He had used this method with larger quantities of fluorine, and for water it would only be necessary to concentrate the fluorine by evaporation. He believed the salt industry in Essex was very old, and it would be of interest to know if mottled teeth had been noticed before the last 100 years or whether they were comparatively recent.

Mr. E. HINKS asked whether all forms of fluoride would act in the same way in this test. If there were silicofluoride, would that react in the same way as a simple fluoride?

Dr. H. E. COX asked whether any effect on the bones or other constituent parts of the body had been noticed at the *post-mortem* examination of persons with mottled teeth.

Dr. BARR, replying, said that they had determined the fluorine in only five samples of Maldon waters; these had been furnished by Mr. Ainsworth, and were found to contain from about 1 to 5 parts of fluorine per million. According to the analyses supplied, the content of sodium chloride was of the order of 50 grains per gallon, so that the maximum ratio of fluorine to chlorine was nearly 1.2×10^{-2} . The average ratio F/Cl reported by Thompson and Taylor (*loc. cit.*) for samples taken in the open sea, at depths of from 0 to 2500 metres, was only 7.0×10^{-5} , and they remarked that much higher ratios were found in inland waters. As the ratio for the Maldon water was 170 times as great as that for sea-water, it was not likely that the fluorine-content was due to infiltration from the sea. Thompson and Taylor gave a list of substances which definitely did not interfere with the determination when present in amounts likely to occur in sea-water; these included iron, carbonates, sulphates, bromides, and iodides. It was probable that a suitable technique could be devised to make the method applicable to food-stuffs. The authors had not tried the process with silicofluorides; according to Robertson, Marriott and Humphreys (*J. Soc. Chem. Ind.*, 1934, 54, 83r) the reaction mixture should be warmed to 70° C., and allowed to cool before comparison of the colours if silico-fluorides were present.

Mr. AINSWORTH, replying, said that the condition of mottled teeth occurred mainly in Arizona. It was found in a few scattered districts in North and South Dakota and Tennessee, but it was practically unknown in the Eastern States of America. He had no knowledge of the effect of traces of fluorine on the body, but the bones of rats which had been given a high proportion of fluorine looked white

and patchy. With regard to the point raised by Mr. Sage, mottling of teeth was produced only in teeth in course of formation. All the photographs shown were those of children; in the particular school which these children attended, the teeth of 80 per cent. of the children were mottled. Adults who came into the district were not affected.

The Analysis of Green Teas

By THOMAS McLACHLAN, F.I.C., AND MARGARET IDA STERN, B.Sc., F.I.C.

OWING to a dispute concerning the ash of a sample of gunpowder tea a short time ago we had occasion to search the literature for figures and found that, while many are published for black teas, few are available for the green variety. Having a collection of samples in the laboratory, we thought that it might be of service to examine these and place the results on record. In doing this we have not used new methods; in fact, in our opinion, one of the disadvantages of many published figures is the use of new methods by authors. It may, however, be well to state briefly the methods we have employed:—

Moisture.—Two grms. of the semi-powdered tea were dried in a flat weighing bottle in an electric oven at 100° C. for 1 hour, cooled and weighed. The sample was re-heated for half-hour periods until constant in weight.

Ash.—One grm. was ashed in a platinum capsule at as low a temperature as possible over a Bunsen or Argand burner. The ash was extracted with 30 ml. of boiling water, the extract was filtered through a small filter, and the residue was washed with boiling water until about 100 ml. of filtrate had been collected. The filtrate was cooled rapidly and titrated with *N*/10 hydrochloric acid, first with phenolphthalein and then with methyl orange as indicator. The ash insoluble in water was treated with 15 ml. of boiling dilute (1 : 1) hydrochloric acid to obtain the acid-insoluble portion. The residue was treated with hydrofluoric and sulphuric acids to separate silica.

Water Extract.—The water extract was determined by the method of Tatlock and Thomson (ANALYST, 1910, 35, 103).

Tannin.—This was estimated by the Löwenthal-Procter method (Leach, *Food Inspection and Analysis*, 4th Ed., p. 383).

Caffeine.—Caffeine was determined by the Bailey-Andrew method (*Official and Tentative Methods of the Assoc. Offic. Agric. Chem.*, 3rd Ed., p. 155).

Unfortunately, there was insufficient material available to enable us to complete the analysis of every sample. Sow Mee is a broken tea, rather better than dust; the other varieties require no explanation.

A suggestion was made that the high ash figures might be due to "facing" with talc, and considerable attention has therefore been given to this question. According to the literature, the amount of talc employed for this purpose seldom exceeds 1 per cent., whereas the amount of matter insoluble in hydrochloric acid is considerably above this figure in most of our samples. It was noticed that every sample of gunpowder tea, except Nos. 6 and 7, appeared to have been

Sample	Gunpowder														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Moisture, per cent.	0.03	9.14	8.89	8.56	9.83	7.96	7.62	8.55	7.99	8.35	8.43	8.04	9.56	9.25	8.61
Extract, per cent.	53.1	51.7	50.3	48.4	54.3	56.6	55.6	52.9	56.3	48.8	48.8	54.3	51.7	53.1	54.2
Total ash, per cent.	8.1	8.1	9.1	9.2	8.0	6.1	5.60	8.6	8.0	8.49	9.70	9.96	10.16	10.3	5.5
HCl required for neutralisation of water-soluble ash from 1 gm. (phenolphthalein), ml. N/10	0.95	0.45	0.6	0.6	0.7	0.7	1.05	0.25	0.64	0.60	0.95	0.70	0.85	0.9	0.6
HCl required for neutralisation of water-soluble ash from 1 gm. (methyl orange), ml. N/10	3.3	2.75	2.9	2.5	3.0	3.1	3.50	1.7	2.7	3.15	3.15	2.15	3.25	2.85	2.8
Ash soluble in water, per cent.	4.3	3.6	2.4	2.3	3.8	4.0	3.75	3.1	3.7	3.74	3.35	3.39	3.05	2.55	3.6
Ash insoluble in water, per cent.	3.8	4.5	6.7	6.9	4.2	2.1	1.85	5.5	4.3	4.75	6.35	6.57	7.11	7.75	1.9
Ash insoluble in water, soluble in 50 per cent. HCl, per cent.	2.6	2.8	4.3	3.2	2.3	1.8	1.6	2.8	2.3	3.01	3.27	3.42	3.38	4.50	1.52
Ash insoluble in HCl, per cent.	1.2	1.7	2.4	3.7	1.9	0.3	0.25	2.7	2.0	1.74	3.08	3.15	3.73	3.25	0.38
Ash insoluble in HCl, less silica, per cent.	0.4	0.4	0.5	1.0	0.3	0.2	0.10	0.8	0.5	0.56	0.93	1.11	1.3	1.95	0.1
Silica, per cent.	0.8	1.3	1.9	2.7	1.6	0.1	0.15	1.9	1.5	1.18	2.15	2.04	2.43	1.3	0.28
Tannin, per cent.	10.52	7.69	6.90	9.37	8.59	9.70	10.58	12.40	13.35	12.49	7.37	9.91	7.86	9.00	—
Caffeine, per cent.	2.10	2.17	—	2.20	2.27	3.37	3.23	2.08	2.73	1.98	—	2.67	2.17	2.20	—

Sample	Sow Mee											Japanese green			Suey		Kee-mum	Oo-lono
	1	2	3	4	5	6	7	8	9	10	11	1	2	3	1	2		
Moisture, per cent.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33
Extract, per cent.	8.34	9.23	9.39	9.45	8.91	8.54	8.64	9.08	8.69	8.84	8.17	7.56	6.92	6.42	9.46	9.83	9.95	8.99
Total ash, per cent.	52.3	49.4	48.5	48.3	53.3	52.3	48.1	50.5	49.7	49.6	48.3	52.5	45.4	53.4	46.3	45.5	52.0	54.3
HCl required for neutralisation of water-soluble ash from 1 gm. (phenolphthalein), ml. N/10	7.6	9.05	9.06	8.94	8.2	5.93	7.62	9.52	7.95	10.85	8.45	6.87	8.9	7.9	6.37	5.93	5.75	6.57
HCl required for neutralisation of water-soluble ash from 1 gm. (methyl orange), ml. N/10	1.3	0.70	0.60	0.70	0.65	0.80	0.45	0.50	1.1	0.4	0.65	0.8	1.4	1.6	0.55	0.95	1.1	0.65
Ash soluble in water, per cent.	3.5	2.15	2.65	2.35	3.25	3.35	2.75	2.85	3.7	1.9	3.15	3.65	3.1	3.3	3.25	3.25	3.65	3.15
Ash insoluble in water, per cent.	3.7	2.60	3.27	3.48	3.29	3.33	3.04	3.48	3.65	3.35	3.35	3.8	3.3	3.2	3.57	2.5	3.95	3.35
Ash insoluble in water, soluble in 50 per cent. HCl, per cent.	3.9	6.45	5.79	5.46	4.91	2.60	4.58	6.04	4.3	7.5	5.1	3.07	5.6	4.7	2.8	3.43	1.8	3.22
Ash insoluble in HCl, per cent.	2.8	4.48	3.88	3.61	2.95	2.25	3.30	3.22	2.3	4.1	2.8	1.85	3.0	2.95	2.4	2.93	1.35	2.20
Ash insoluble in HCl, less silica, per cent.	1.1	1.97	1.91	1.85	1.96	0.35	1.28	2.82	2.0	3.4	2.3	1.22	2.6	1.85	0.40	0.50	0.45	1.02
Silica, per cent.	0.4	0.46	0.60	0.60	0.90	0.15	0.43	0.92	0.8	1.2	0.8	0.37	1.0	0.75	0.15	0.1	0.17	0.3
Tannin, per cent.	0.7	1.51	1.31	1.25	1.06	0.2	0.85	1.90	1.2	2.2	1.5	0.85	1.6	1.1	0.25	0.4	0.28	0.72
Caffeine, per cent.	9.54	6.48	6.30	—	9.00	9.0	7.74	8.56	6.84	5.70	7.2	8.77	8.37	9.60	5.77	3.98	7.34	11.04
—	—	2.03	1.83	—	2.20	2.03	2.2	—	2.17	—	1.77	2.73	2.18	2.52	2.58	2.3	3.83	2.42

"faced" with talc, but it was found impossible to remove this by shaking with water, as suggested in the literature. When attempts were made to remove the talc, it was found that other mineral matter was removed at the same time. The ash insoluble in hydrochloric acid from every sample was examined microscopically and gave the impression at first that, in all but one or two samples, talc was present. This seemed unreasonable, since talc would be expensive as a loading material and could not account for the high amount of matter insoluble in water, but soluble in hydrochloric acid. The particles of siliceous matter insoluble in hydrochloric acid were extracted from a piece of the Great Wall of China in our possession and, when examined microscopically, showed a structure almost identical with that present in most of our samples. The silica from very fine sand was very similar, as were also the silicates insoluble in hydrochloric acid from Cornish china clay and fuller's earth, but that present in powdered pumice (passing a 180-mesh sieve) was considerably more angular.

It is, therefore, concluded that there is no apparent reason to think that the ash of green tea need really be much greater than that of black tea, although there does not appear to be any method of checking it at the moment. At the same time, it is our opinion that the high ash is due, in the main, to extraneous dirt, rather than to actual "facing."

In view of the suggestion in the paper of Tatlock and Thomson (*ANALYST*, *loc. cit.*), that China teas contain an excess of caffeine, as against the high tannin-content of black teas, it is interesting to note that our results do not enable us to draw any such inference.

Micro-Volumetric Determination of Sulphur and Chlorine in Organic Compounds with the Use of an Assay Balance

BY DOUGLAS W. COWIE AND DAVID T. GIBSON

THE simple micro-volumetric method described by Pregl (*Quantitative Organische Mikroanalyse*, 3rd Ed., p. 163) for determining sulphur in compounds free from nitrogen and halogen can be extended to the determination of sulphur and halogen by absorbing the combustion gases in standard alkali. The total acidity is determined, the solution concentrated, and the halide content determined by Volhard's method.

Unfortunately, we were limited to the use of an assay balance reading to 0.01 mgrm., but the following table (which gives a series of 36 unselected analyses) shows that the method is capable of results within the usually accepted limits. The analysis takes 3 to 4 hours and requires 4 to 6 mgrms. of substance.

Working from right to left the apparatus, as far as V, is the same as recommended by Pregl for the determination of sulphur, except that certain simple modifications greatly increase its reliability.

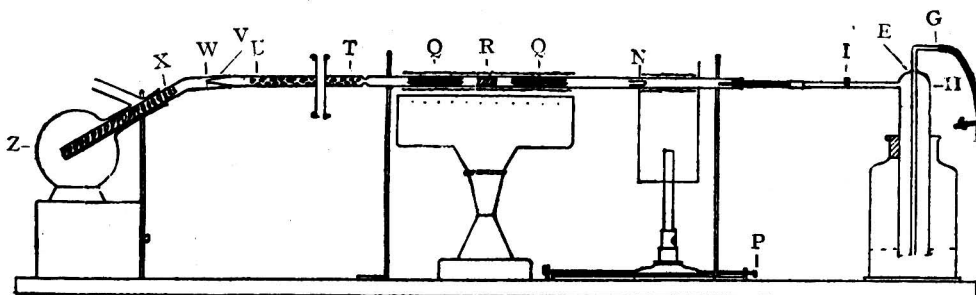
(i) E is a glass seal, thus ensuring the relative levels of the inner (G) and outer (H) tubes. Pregl's cork joint is liable to slip gradually. The tube (H) has a lip, like a beaker, to facilitate the escape of any excess pressure.

(ii) The substance is contained in a hard glass tube (N) (not a boat); combustion is more even and danger of flashing is minimised.

(iii) Between the platinum contacts Q, Q' a short piece of silica, R, wound round with platinum wire ensures a more thorough mixing of the gases.

(iv) We find it a great advantage to terminate the filling so as to leave an empty space, UV. The capillary end, V, is otherwise liable to be sealed by a drop of liquid. Since introducing this feature we have never been troubled with this.

(v) The movable Bunsen burner is much more evenly advanced if it is mounted on a screw, P.



Such an apparatus retains sulphurous gases completely when the glass spirals, T, are moistened with water; but halogens, as Pregl found, can be retained only by alkali. As it was impracticable to moisten the glass spirals with an exact amount of alkali, we have added the guard tube, WX, which, together with the flask, Z, is moistened with 5 ml. of N/50 sodium carbonate solution. The guard tube fits over the main combustion tube, and the joint is made gas-tight with a drop of water.

The combustion is carried out exactly as described by Pregl (3.5 ml. oxygen per minute being a convenient speed).

TABLE I

(CHLORINE IN SULPHUR-FREE COMPOUNDS)

Substance	Chlorine found, per cent.		
	Alkali	Silver nitrate	Theory
Chloro-camphor ..	19.0	19.0	19.0
	19.1	19.0	
<i>p</i> -Dichlorobenzene ..	48.0	47.8	48.3
	47.8	48.0	
	47.8	47.9	

When the combustion is completed, tap I is closed and the guard tube disconnected. This tube is washed clean with 20 ml. of distilled water from a wash-bottle with a very fine jet. The main combustion tube is then washed out with a further 15 ml. of distilled water, and one drop of perhydrol is added to the combined

washings in the flask, which is allowed to stand for ten minutes. Perhydrol not only oxidises any sulphite, but reduces oxy-acids of chlorine to chloride (Viebock, *Ber.*, 1932, 586). The solution is then boiled vigorously for two minutes and cooled, one drop (= 0.03 ml.) of a mixed methylene blue and methyl red indicator is added, and the solution is titrated with *N*/100 sulphuric acid until the green colour

TABLE II
(SULPHUR AND CHLORINE)

Substance	Chlorine, per cent.		Sulphur, per cent.	
	Found	Theory	Found	Theory
Ethyl- α -chlorocamphor-10-sulphonate	12.1 12.0	12.1	10.6 10.6	10.9
$\text{Cl}_2\text{C}_6\text{H}_3\text{SO}_2\text{SC}_6\text{H}_3\text{Cl}_2$	36.3 36.5		36.6	
$\text{ClC}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{Cl}$	21.6 22.2 22.2	22.3		19.6 20.0 19.9
$\text{ClC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{COCH}_3$	15.4 15.3		15.3	13.7 13.8
$(\text{ClC}_6\text{H}_4)_2\text{SO}_2$	24.2 24.7	24.7		11.2 10.9
* $(\text{C}_2\text{H}_5\text{SO}_2)_2\text{CCl}_2$	23.9		26.4	24.0
$\text{ClC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{COCH}_3$	15.3	15.3	13.6	13.8
$(\text{ClC}_6\text{H}_4)_2\text{SO}_2$	24.7	24.7	11.0	11.2
$(\text{C}_2\text{H}_5\text{SO}_2)_2\text{CCl}_2$	26.6 26.5	26.4	23.9 24.1	23.8
$\text{ClC}_6\text{H}_4\text{SO}_2\text{CH}_3$	19.0		18.6	
$\text{ClC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{COCH}_3$	15.0 15.0	15.3	13.9 13.8	13.8
$\text{Cl}_2\text{C}_6\text{H}_3\text{S}\cdot\text{SC}_6\text{H}_3\text{Cl}_2$	39.6 39.6		39.9	
$(\text{ClC}_6\text{H}_4)_2\text{SO}_2$	24.9 24.9	24.7		11.4 11.3
$\text{ClC}_6\text{H}_4\text{SO}_2\text{CH}_3$	19.0 18.9		18.6	17.0 17.0
$(\text{C}_2\text{H}_5\text{SO}_2)_2\text{CCl}$	9.7 9.5	9.5		25.6 25.6
$(\text{C}_6\text{H}_5\text{SO}_2)_2\text{CCl}$	9.5			
$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	18.6 18.8	18.6	17.1 17.1	16.8
$\text{Cl}_2\text{C}_6\text{H}_3\text{SO}_2\text{Cl}$	43.3 43.7		43.4	
$\text{CH}_3\text{C}_6\text{H}_3(\text{OCH}_3)\text{SO}_2\text{Cl}$	16.2 16.2	16.1		14.3 14.6
$\text{C}_{10}\text{H}_7\text{SO}_2\text{Cl}$	16.0 15.9		15.7	14.1 14.0

* Compound subsequently found to be impure.

disappears. The solution is again heated to boiling, and cooled, and more standard acid is added until the colour swings from an intense green to a definite violet with one drop of acid. It is necessary to boil the liquid, as the indicator is affected by the presence of carbonic acid, but the actual end-point is much sharper in a cold solution.

The solution, which is contained in a 100-ml. quartz distilling flask, is then heated on a water-bath while a stream of filtered air is drawn over the surface. In an hour 60 ml. are thus reduced to 10 ml. This concentrated solution is titrated with silver nitrate (1 ml. = 0.5 mgrm. of chlorine) until no further turbidity is observed, filtered and back-titrated with thiocyanate solution. If the solution is not concentrated, it is very difficult to observe the end-point; and if too much silver nitrate is used, the excess tends to be occluded, so that rather high results are obtained.

UNIVERSITY OF GLASGOW

The Determination of Zinc in large Quantity, with particular reference to the Analysis of Brass

BY L. C. NICKOLLS, M.Sc., D.I.C., A.I.C., AND J. G. N. GASKIN,
B.Sc., F.I.C.

THE analysis of alloys containing high percentages of zinc is rendered difficult by the lack of methods suitable for determining this metal accurately in the quantity usually taken for analysis. For example, 2 grms. of brass contain 0.6 to 0.8 gm. of zinc, but for the accurate determination of this quantity there appears to be, at present, no convenient method, so that the zinc-content is frequently reported as a difference figure, or by a determination on a weighed aliquot part of the solution of the metal. Neither of these methods being entirely satisfactory, we have examined and tested the standard methods for the determination of zinc, with a view to adapting the most suitable to the determination of the total zinc-content of alloys such as brass.

PRELIMINARY EXPERIMENTS.—Three methods have been examined. In the preliminary experiments a 50-ml. portion of a sulphuric acid solution of 10 grms. of zinc in a litre was taken. Later experiments were made on weighed aliquot parts of a solution twice this strength.

Method I (Precipitation as zinc ammonium phosphate and ignition to pyrophosphate).—The conditions for quantitative precipitation are critical. The precipitate is easily filtered in a Gooch crucible and ignited, but the results are consistently high.

Zinc taken Grm.	Zinc found Grm.
0.5002 (volume)	0.5058
	0.5064
	0.5070
0.5002 (weight)	0.5021
	0.5044

Method II (Precipitation as zinc pyridine thiocyanate and ignition to oxide).—The precipitate obtained from 0.5 gm. of zinc was excessively bulky and difficult

to handle. After prolonged ignition it contained varying proportions of carbon, zinc sulphide and zinc sulphate.

Zinc taken Grm.				Zinc found Grm.
0.5002 (volume)	0.5066
				0.5050
				0.5048
0.5002 (weight)	0.5046

Method III (Electrolysis of the zinc in alkaline solution).—Of the three methods, this is the simplest in operation, and the results obtained showed that it is the most accurate.

Zinc taken Grm.				Zinc found Grm.
0.5002 (volume)	0.5015
				0.5031
				0.5022
0.5002 (weight)	0.5008
				0.5010
				0.5007

Method III was accordingly selected as the most suitable for our purpose.

INVESTIGATION OF METHOD III.—It is well known that zinc is deposited on the cathode when an alkaline solution of this metal is electrolysed. Further, it is well known that nitrates and ammonium salts prevent this deposition. We have confirmed this; traces of nitrates hinder the deposition, and small quantities entirely prevent it. It is also recorded that at temperatures in excess of 20° C. the zinc is not deposited. We have found that, even if deposited at about this temperature, the zinc may easily re-dissolve as the solution becomes warmer. At low temperatures (0° C.) the deposit is firm and closely adherent. In our experiments, therefore, the vessel containing the electrolyte was immersed in an ice-bath. With a rotating gilt platinum cathode, and a current density of 0.035 amp. per sq. cm., 1 gram. of zinc was deposited in an hour and a half at this temperature.

In our first experiments the cathode, having been washed thoroughly with water, was dipped in alcohol and dried at 100° C. for 5 minutes. This gave high results, obviously, as appearance indicated, owing to surface oxidation.

				Per Cent.
Zinc found (alcohol drying)	36.77
				36.79
Zinc present (from analysis)	36.60

Later, acetone was substituted for the alcohol, and the cathode was dried in the steam-oven for less than a minute. The resultant deposit showed no signs of surface oxidation. When the electrolysis is properly carried out the whole of the zinc is deposited, and no traces are left in the solution.

APPLICATION OF METHOD III TO THE ANALYSIS OF BRASS.—To apply the electrolysis of zinc to the analysis of brass required some consideration of the salts likely to be present in the solution. From what has been said it is obvious that the removal of copper by electrolysis in nitric acid solution must be followed by

some operation designed to remove the nitric acid. For this purpose tests were made with metallic aluminium. Reduction with aluminium carried out in a warm alkaline solution proved adequate to remove the nitric acid as ammonia, the last traces of which could then be removed by boiling. This, however, led to a further difficulty, inasmuch as at least 6 grms. of aluminium were necessary to remove the nitric acid in a normal analysis of brass, and this quantity of aluminium, particularly in the presence of tartaric acid, rendered it difficult to deposit the whole of the zinc, and, further, had a slightly adverse effect on the nature of the deposit.

This procedure was, therefore, abandoned in favour of an attempt to make a separate determination of the zinc in hydrochloric acid solution. Electrolysis of the zinc is unaffected by the presence of alkali chlorides. The brass was, therefore, dissolved in a mixture of hydrochloric acid and the minimum quantity of nitric acid, and the acids were removed by evaporation to dryness. It remained, then, to remove the copper in the solution obtained after the addition of water to the dry chlorides. It was found that aluminium, in the practically neutral solution, completely replaced the copper, leaving a coagulated precipitate, easily filtered. The best results were obtained when the replacement took place in a hot solution, which was continuously agitated to displace the precipitated metal from the surface of the aluminium. The solution being, moreover, nearly neutral, no copper was re-dissolved, and unnecessary quantities of aluminium in solution were avoided. If the replacement takes place in the cold, some cuprous salts are formed by reduction, and it is impossible subsequently to convert these salts into metallic copper. One grm. of aluminium was found to be more than sufficient to replace all the copper when 2 grms. of brass were used for the determination.

Tin and other possibly interfering elements are dealt with after the description of the method which follows:—

METHOD FOR THE DETERMINATION OF ZINC IN BRASS.—Two grms. of brass, in the form of fine drillings, are dissolved in a mixture of 10 ml. of water, 7 ml. of concentrated hydrochloric acid and 3 ml. of concentrated nitric acid. This solution is evaporated nearly to dryness, after which a little bromine is added and the evaporation is continued to dryness on the water-bath. The salts are dissolved in 50 ml. of hot water and 5 grms. of anhydrous sodium sulphate are added. To the hot solution are added two pieces of aluminium foil, each about 0.5 grm. in weight, and the replacement of the copper is allowed to proceed as rapidly as possible, the contents of the beaker being agitated with a rod throughout the operation. The solution is left in contact with the aluminium for one hour, after which it is cooled and filtered, and the precipitate is then well washed with cold water. Fresh 50 per cent. sodium hydroxide solution is added to the filtrate until the precipitates of zinc and aluminium are re-dissolved, and any small precipitate is then removed by filtration.* Otherwise a further quantity of sodium hydroxide is added to the solution to give an excess equivalent to 20 ml. of 50 per cent. caustic soda. This solution is electrolysed by means of a rotating gilt platinum cathode, the beaker containing the electrolyte being placed in an

* Copper left in solution will appear at this stage as a yellow precipitate, and, since its removal is difficult, it is best, unless the quantity is quite small, to make a fresh determination.

ice-bath. Electrolysis is carried on for an hour and a half, with a current density of 0.035 amp./cm², the electrodes being about 2 cm. apart; after this the whole of the zinc should have been deposited. The cathode is removed with the current still running, washed thoroughly with cold water, dipped in acetone and dried for half a minute in a steam-oven, cooled and weighed. The electrolyte should be examined for any traces of zinc by passing hydrogen sulphide through the liquid; but, if electrolysis has been correctly carried out, zinc should be absent.

EFFECT OF OTHER METALS AND THE MODIFICATION IN PRESENCE OF IRON.—When iron or manganese is present in quantities greater than 0.05 per cent., it is advisable to adopt a modified procedure after the removal of the copper, since some zinc is invariably co-precipitated by sodium hydroxide with the iron and manganese hydroxides.

The solution is oxidised with bromine, treated with sodium hydroxide as before, and heated to boiling, and the iron and manganese hydroxides are removed by filtration. These are dissolved in hydrochloric acid and re-precipitated with ammonia. After filtration, any zinc in the filtrate may be recovered by any of the standard methods, or, alternatively, an excess of sodium hydroxide is added, the ammonia removed by boiling, the solution returned to the main bulk, and all the zinc electrolysed in one operation.

The presence of small quantities of lead, tin, nickel or magnesium does not affect the accuracy of the method.

Tin is partly volatilised as stannic chloride during the first evaporation, but most of it is removed as insoluble metastannic acid during the filtration of the copper precipitate, the first evaporation having the twofold purpose of removing the nitric acid and fixing the tin. Similar remarks apply to the small quantities of arsenic commonly found in brass.

The addition of sodium sulphate, after the evaporation to dryness, precipitates most of the lead present, and this is, therefore, also removed during the filtration of the copper. Any traces remaining in solution are removed as carbonate by filtration of the alkaline solution.

It was observed that nickel behaved similarly to copper and was completely replaced by aluminium.

Magnesium is largely removed as oxychloride during the filtration of the copper, but traces remaining in solution are precipitated later as hydroxide and may be removed by filtration of the alkaline solution.

EXPERIMENTAL RESULTS.—The above method was successfully applied to a sample of brass having the following composition:—

					Per Cent.
Copper	61.67
Tin	1.29
Lead	0.41
Iron	nil
Arsenic	0.03
Zinc (by difference)	36.60
					<hr/> 100.00 <hr/>

The following percentage results were obtained for the zinc-content:—
36.65, 36.66, 36.54, 36.64 36.53.

We have to thank Sir Robert Robertson, K.B.E., F.R.S., for permission to publish this paper.

GOVERNMENT LABORATORY

CLEMENT'S INN PASSAGE, STRAND, W.C.2

The Determination of Bismuth in Copper

BY E. W. COLBECK, M.A., S. W. CRAVEN AND W. MURRAY

INTRODUCTION.—In view of the uncertainty of many of the methods for the chemical separation of small amounts of bismuth from copper, a new method has been evolved depending on the formation of a bismuth mirror when copper millings are heated at 1050–1060° C. in a stream of hydrogen.

According to F. Paneth (*Ber.*, 1918, **51**, 1704), a gaseous bismuth hydride can be formed which is comparatively stable at ordinary temperatures, but is decomposed at high temperatures. F. Paneth and E. Winternitz (*loc. cit.*) obtained the hydride from a bismuth-magnesium alloy in sufficient quantities to permit of its detection by the formation of a mirror or by luminescence tests. If such a hydride could be obtained, it would afford a means of separation of bismuth from copper, since, according to the literature, the latter element does not form a hydride.

A separation need not necessarily depend upon the formation of a bismuth hydride, since it is possible that above a certain temperature bismuth might distil in an atmosphere of hydrogen, whilst no distillation would take place below this critical temperature. A paper published by T. G. Pearson, P. L. Robinson and E. M. Stoddart (*Proc. Roy. Soc.*, 1933, [A], **142**, 275) suggests that this alternative is more probable. In either case deposition of metallic bismuth should take place at some point in an enclosed system.

Experimental work showed that bismuth could be separated quantitatively from copper by heating in a stream of hydrogen. The following method embodies the conditions that have been found most satisfactory:

APPARATUS.—The apparatus required is as follows:

A horizontal electrically-heated tube furnace, 24 in. long, capable of being maintained at 1060° and fitted with a thermo-couple for the measurement of the temperature of the middle of it.

A clear silica combustion tube 36 inches long, 7/8 in. internal diameter drawn out at one end to 1/4 in. diameter.

Fire-clay combustion boats, as used in the determination of carbon in steel.
A supply of hydrogen gas and a suitable flow-meter.

PROCEDURE.—A portion of the sample of copper, in the form of fine turnings or millings, is weighed out into a fire-clay boat, which is then introduced into

the centre of the coal-furnace. Hydrogen at the rate of about 18 litres per hour is passed over the sample; when all the air is expelled from the tube the escaping gas is ignited. The temperature of the furnace is then raised to 1060°C ., and maintained there for 1 hour. At the end of this time the furnace current is switched off, the rubber at the end of the silica tube is detached, the hydrogen supply is cut off, and the bung at the entry end of the silica tube is removed. A small explosion occurs, after which the boat is extracted, and the silica tube is removed from the furnace and allowed to cool. The drawn-out exit end is then stoppered by means of a glass rod attached to it by rubber tubing, and the bismuth mirror is dissolved off with concentrated nitric acid. Very little acid is required for this purpose, and the amount used should always be so regulated that 100 ml. of the resulting solution does not contain more than 2 ml. of concentrated acid. The tube is washed out with distilled water, the solution is made up to a known volume, and an aliquot portion is taken, the bismuth content of which should not exceed 0.0004 gm.

This aliquot portion is placed in a Nessler cylinder, 6 drops of an aqueous solution of sulphur dioxide (1 vol. of a saturated solution with 3 vols. of water) and 5 ml. of a 2 per cent. aqueous solution of potassium iodide are added. The same volumes of these reagents and a volume of nitric acid equal to that present in the test solution are introduced into a second Nessler cylinder. The volumes in both cylinders are made up to 100 ml., and the standard bismuth solution, containing 0.0001 gm. of bismuth per 1 ml., is added to the second cylinder until the colours match.

After the determination, starch solution is added to both tubes to make sure that the colours are not caused by free iodine. If a blue colour is obtained, the determination should be repeated, a larger volume of sulphur dioxide solution than is specified above being used. The standard bismuth solution is made by dissolving bismuth metal in nitric acid.

When it is impossible to obtain fine millings (*e.g.* granulated copper), the temperature must be raised above the melting-point of the sample, *i.e.* to $1100\text{--}1120^{\circ}\text{C}$. After the expiration of one hour the furnace should be allowed to cool, the hydrogen stream being maintained until the temperature has fallen well below 1084°C . In this way spitting of copper is prevented.

EARLY EXPERIMENTAL WORK.—That bismuth can be separated from copper in a stream of hydrogen was shown in the following preliminary experiment:—An intimate mixture of a known weight of electrolytic copper and a known weight of finely-divided bismuth metal was made, placed in a boat, and heated in a stream of hydrogen at 1050°C . A mirror, readily soluble in nitric acid, was formed about 9 inches from the boat. A colorimetric determination of bismuth in this solution showed that this mirror contained the whole of the added bismuth. Bismuth added, 0.0142; found, 0.0145 per cent.

This experiment was repeated on a known weight of pure bismuth oxide instead of bismuth metal, with the following result:—Bismuth oxide added, 0.0076 gm.; found, 0.0077 gm. (determined as Bi). The hydrogen used in the above experiment was taken straight from a gas cylinder to the furnace. Two similar determinations were carried out in which hydrogen, dried by passing

through calcium chloride and phosphorus pentoxide drying tubes, was used. Quantitative separation of the bismuth was again effected in both cases.

Samples of copper containing bismuth were treated in a similar manner; in every instance a deposit similar to that described above was obtained in the same place on the tube.

ESTABLISHMENT OF THE METHOD.—To show that the method was quantitative, the following procedure was adopted. Sufficient copper millings to make a small ingot were treated for the removal of bismuth by the mirror method. The residues left in the boat were allowed to cool to room temperature in a stream of hydrogen to prevent oxidation, and were afterwards melted in a H.F. induction furnace. A representative sample was taken from the ingot for analysis. The remaining portion was weighed and re-melted and a known weight of bismuth metal was added. The bismuth melted readily without any signs of loss, such as fuming, and the melt was super-heated just sufficiently to allow it to be tapped. Since the high-frequency currents induced in the molten-copper have a most pronounced stirring effect, a homogeneous ingot is obtained. There was no loss in weight during melting. A representative sample for analysis was taken from the second ingot. Analytical results are given in Table I:

TABLE I

Ingot	Addition made	Bismuth found by mirror method Per Cent.
Re-melted residues	None	Less than 0.0002
Re-melted residues plus a known weight of bismuth (metal)	0.0106 per cent. of bismuth as the metal	0.0105

For purposes of comparison these two samples were analysed for bismuth by the method depending upon the co-precipitation of bismuth carbonate with calcium carbonate. The results are given in Table II:

TABLE II

Ingot	Additions made	Bismuth found by co-precipitation method Per Cent.
Re-melted residues	None	Trace
Re-melted residues plus a known weight of bismuth (metal)	0.0106 per cent. of bismuth as the metal	0.0075 per cent.

Two samples of electrolytic copper, supplied by I.C.I. (Metals), Ltd., were examined by the mirror method, and found to contain 0.0015 per cent. and 0.0020 per cent. of bismuth, respectively. These amounts of bismuth are much higher than the maximum allowed for this type of copper under British Standard Specification No. 198 (1925). The two electrolytic copper samples were also analysed by the co-precipitation method, and were found to contain 0.00016 per cent. and 0.00015 per cent. of bismuth. In view of this high figure for bismuth in electrolytic copper as determined by the mirror method, it is of interest to note that a sample of vacuum-melted copper was tested by this method and found to contain 0.001 per cent. of bismuth.

In further tests on the mirror method as compared with the method depending on the co-precipitation with calcium carbonate, a series of copper ingots was prepared. Electrolytic copper was used as a base metal, and known weights of bismuth metal were added to it. The results are shown in Table III:

TABLE III

Ingot number	Bismuth added Per Cent.	Mirror method		Co-precipitation method	
		Bismuth, theoretical Per Cent.	Bismuth found Per Cent.	Bismuth, theoretical Per Cent.	Bismuth found Per Cent.
Electrolytic copper (base)	—	—	0.0015	—	0.00015
			0.0016		0.00015
S.1	0.00483	0.0064	0.0058 0.0058	0.0050	0.0043 0.0047 0.0046
S.2	0.00953	0.0111	0.0098 0.0100	0.0097	0.0083 0.0084 0.0087
S.3	0.0483	0.0499	0.0500 0.0495	0.0485	0.043 0.046
S.4	0.0968	0.0984	0.098 0.098	0.097	0.086 0.086

In the above table the theoretical bismuth percentage is equal to the percentage of bismuth metal added plus the percentage of bismuth found by the method in question.

It will be observed that in all four cases the mirror figures are much closer to the theoretical values than those of the co-precipitation method. In S.1 and S.2 the difference in the percentage of bismuth present in the electrolytic copper, as determined by the two methods, has a considerable influence on the theoretical percentage of bismuth. In S.3 and S.4, however, where the added amounts of bismuth metal are much higher, the figure for the base metal does not influence the theoretical percentage very much. Yet in both S.3 and S.4 the co-precipitation method gives results that are still 10 per cent. below the theoretical amount.

CONSIDERATION OF THE EFFECT OF POSSIBLE IMPURITIES.—Of the impurities likely to be present in copper, arsenic and antimony, owing to the readiness with which they form hydrides, are the elements likely to interfere with the determination of bismuth by the mirror method. To investigate the possibility of such interference, samples having a known percentage of bismuth and containing also arsenic and antimony were analysed. The results are given in Table IV:

TABLE IV

Sample mark	Bismuth theoretical Per Cent.	Additions	Bismuth found by the mirror method Per Cent.
S.8	0.0175	None	0.0170
S.7	0.0174	0.001 per cent. of antimony	0.0170 0.0170 0.0168
S.11	0.0213	0.018 per cent. of arsenic	0.0199

Apparently, therefore, neither arsenic nor antimony has any serious effect on the accuracy of the results obtained by the mirror method.

Our thanks are due to the Directors of Imperial Chemical Industries, Limited, for permission to publish this work, which was carried out in the Research Department of their subsidiary company—I.C.I. (Alkali), Ltd., Northwich.

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.

THIOCYANOGEN VALUES OF SOME EGYPTIAN SESAME AND COTTON-SEED OILS

THE thiocyanogen values of some Egyptian vegetable oils were determined by the method described by Kaufmann (ANALYST, 1926, 51, 157; 1928, 53, 613).

The results, and the proportion of esters of saturated acids calculated from the formula

Esters of saturated acids = $100 - 1.16 \times$ thiocyanogen value
are given below.

SESAME OIL

Thiocyanogen value	74.5	74.4	76.1	74.3	74.4	75.5	74.5	74.8	74.6	74.9	75.5
Esters of satd. acids	13.6	13.7	11.7	13.8	13.7	12.4	13.6	13.2	13.5	13.1	12.4

COTTON-SEED OIL

Thiocyanogen value	63.2	64.8	64.3	63.4
Esters of saturated acids	26.7	24.8	25.4	26.5

It should be noted that the reagent does not keep for more than three days; low results are obtained after this period. When 50 ml. of the reagent and 0.1–0.12 gm. of oil are used, the amount of thiocyanogen absorbed is equivalent to 5 or 6 ml. *N*/10. As the margin of error is about 0.05 ml. *N*/10 thiocyanogen in the titration, this error is of the order of 1 in 120 in the result.

H. ATKINSON

LABORATORIES
DEPARTMENT OF PUBLIC HEALTH
CAIRO

THE DETERMINATION OF ARSENIC IN TARTAR EMETIC

A MODIFICATION of the German Pharmacopoeia method for the detection of arsenic in tartar emetic can be made quantitative by colorimetric comparison with standards. Two grms. of the sample are weighed into a colourless test-tube, of about 15 mm. diameter, and 5 ml. of arsenic-free hydrochloric acid are run in. One ml. of stannous chloride reagent (B.P.) is then added, and the solution is heated just to the boiling-point to dissolve the tartar emetic. The tube is then allowed to stand, and the colour which develops is compared, by reflected light, against a sheet of white paper, with standards containing 2 grms. of pure arsenic-free tartar emetic and standard arsenic solution equivalent to 0, 0.015, 0.02, 0.025 mgrms., etc., of arsenic treated in precisely the same way. Certain substances, such as traces of mercuric chloride, accelerate the reduction considerably, and addition to the acid solution of 1 or 2 drops of a 0.01 per cent. solution of mercuric chloride causes separation of the arsenic quickly enough for a comparison of colour to be made after about 15 minutes.

Any potassium chloride that separates can be re-dissolved by adding a few drops of water, or the original hydrochloric acid may be diluted with 10 per cent. of water.

The accuracy of the method is within about 2 parts per million when the arsenic present is not appreciably in excess of the limit of the B.P.; when a large number of samples have to be examined the method is a simple and extremely rapid sorting test.

It is worth noting that samples of tartar emetic belonging to the same consignment contained widely varying proportions of arsenic, the amounts ranging between less than 5 and more than 60 parts per million.

H. ATKINSON

LABORATORIES
DEPARTMENT OF PUBLIC HEALTH
CAIRO

NOTE ON THE DIPHENYLAMINE TEST FOR NITRATES IN MILK AND ITS RELIABILITY IN THE PRESENCE OF SMALL QUANTITIES OF CHLORINE

It is, of course, as Elvidge points out in his note in *THE ANALYST* (1934, 170), well known that this test is not specific for nitrates, but is given by other oxidising agents. The large number of routine tests which we have made, giving no evidence of traces of nitrates or other oxidising agents, however, indicates that interference by these oxidising agents very rarely occurs in practice. Hypochlorite is the oxidising agent most likely to be encountered, but, on theoretical grounds, it appeared to us to be very unlikely that such a reactive substance would persist unaltered in milk in high dilution and give the diphenylamine reaction. We considered it desirable, therefore, to ascertain the limits to which hypochlorite can be detected, (i) in aqueous solution, and (ii) in milk, by the diphenylamine test, and at the same time to establish controls with nitrates under exactly the same conditions. The following results were obtained:

In water

0.1 part per 10^6 of nitrogen, as nitrate (but not less) is detected with certainty
5.0 parts ,, ,, chlorine (but not less) are detected with certainty

In milk

0.25 part ,, ,, nitrogen as nitrates (but not less) is detected with certainty
100 parts ,, ,, chlorine (but not less) are detected with certainty

In milk, 400 times as much chlorine as nitrogen (as nitrates) is required to give the blue colour.

We are, therefore, quite unable to agree with the statement of Elvidge, that 0.1 part per million of chlorine, or anything like so small a quantity, in milk can be detected, and, in our opinion, it is extremely improbable that the diphenylamine test for nitrates in milk will be affected by hypochlorites conveyed to the milk from milking machines, separators, etc., to which it has been applied for cleaning purposes.

In the application of these tests, Lerrigo's technique (ANALYST, 1930, 55, 433) has been adhered to, the time given for the development of colour being not more than half an hour.

It is well known that the presence of the chloride ion is necessary for the detection of very small amounts of nitrates by means of the diphenylamine test; in its presence the test is about ten times as sensitive. In the detection of chlorine the sensitiveness is independent of the presence of the chloride ion; this suggests that the reaction is not the same.

SOMERSET COUNTY LABORATORY
WESTON-SUPER-MARE

D. R. WOOD
E. T. ILLING
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NITRATES IN MILK

OVER forty years ago, the late Mr. H. Droop Richmond published his opinion that cows drinking nitrated water produced milk that gave the diphenylamine test for nitrates (ANALYST, 1893, 18, 279; 1894, 19, 83). Since that time his opinions have been quoted upon many occasions (in depreciation of the value of the detection of nitrates in milk), and most recently by Elvidge (ANALYST, 1934, 170).

In my note ("The Routine Detection of Nitrates in Milk," ANALYST, 1930, 55, 430) I stated that the above opinions were based on faulty manipulation of the test. This statement not only represented my conviction based upon experience, but had the authority of Mr. Richmond himself behind it. I had been in communication with him on the matter, and, in view of the repeated quoting of his early opinions, I have been asked to publish part of the letter which he wrote to me in October, 1929. It reads as follows:—" . . . I may say, however, that at the present time I am by no means convinced that there was not some pitfall in the observation which I made then. The method I was using was to float the milk on a sulphuric solution of diphenylamine, and I can distinctly remember that in the case where I was under the impression that I found nitrate, there was a very slight blue colour produced. I am not, however, now convinced that this blue colour was necessarily due to the presence of nitrates. . . . I think I may say that if I had known as much about the diphenylamine reaction in those days as I do now, I should have been chary in reporting the presence of nitrates."

A. F. LERRIGO

LABORATORY OF THE CITY ANALYST
BIRMINGHAM

NOTE ON NITRATES IN MILK

A PAPER by Elvidge (ANALYST, 1934, 59, 170) refers to the practice of sterilising dairy utensils with hypochlorite solutions, and gives a series of results obtained in the detection of such solutions in milk.

The author states that he was able to detect one part per million of chlorine with ease, and that one in ten millions was just discernible with the diphenylamine test (Lerrigo, ANALYST, 1930, 55, 433). Diphenylbenzidine (Monier-Williams,

ANALYST, 1931, 56, 397) gave a tenfold increase in delicacy, from which it is to be assumed that one part of chlorine in one hundred millions was just discernible.

I have attempted to obtain similar results, but have met with complete failure except with high concentrations. The disinfectant "Milton" was used as a source of hypochlorite and was standardised by arsenite in the usual way.

Quantities of chlorine varying from one in one thousand to one in ten millions were used, and the diphenylbenzidine test was employed in all cases. Positive results were obtained only with concentrations of one in a thousand and one in ten thousand, but the former concentration is so high as to be detectable by its odour, and it renders the milk undrinkable.

Elvidge further states that a concentration of one part of chlorine in ten millions gives a colour about equal in depth to that given by one in ten millions of nitrate. Attempts to repeat this resulted in a very deep blue with the nitrate, but a negative result with the chlorine.

The ortho-tolidine test gave negative results in all cases. Attempts to apply the starch-iodide method of detection similarly proved of no value. With this, a concentration of one in one thousand of chlorine gives an intense blue—as was to be expected, since free chlorine can be detected by its odour. One part in ten thousand liberated iodine, but did not colour the starch blue, giving instead a yellowish colour due, no doubt, to the iodo-protein complex. All other concentrations gave negative results.

W. R. DRACASS

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BUFFERS FOR THE LACTIC FERMENTATION

WHEN pasteurised separated milk is soured with a good starter of lactic streptococci (including aroma bacteria) lactose is fermented, mainly to lactic acid, and the citric acid (average 0.16 per cent.) almost disappears (about 0.03 per cent. is left), yielding volatile acids, the molecular weight of which corresponds with acetic acid (average 0.08 per cent.). The total acidity, volatile acidity and aroma of the culture can often be increased by adding a little citrate to the milk.

If we compare the acidities of milk, diluted milk, and whey, both before and after fermentation, such results as these are obtained:

	Skim milk	75 per cent. skim	50 per cent. skim	25 per cent. skim	Whey
Original acidity.. ..	0.18	0.13	0.08	0.04	0.11
Final acidity	0.92	0.74	0.49	0.27	0.39
Acidity of fermentation	0.74	0.61	0.41	0.23	0.28

The acidity is titrated with *N*/10 alkali (phenolphthalein as indicator), and calculated as lactic acid. In each case only a fraction of the lactose is fermented. The differences in the acidities of fermentation are due mainly to the amount of buffers in the solutions. What is measured is the amount of lactic acidity which the bacteria can produce before the hydrogen ion concentration of the medium is increased from, say, p_H 6.6 to p_H 4.2, though there are minor complications.

If the buffer action of a substance has to be measured, 1 part of skim milk may be diluted with 3 parts of a neutral solution of the buffer, and its fermentation compared with that of a control diluted with water, each having received an addition of 2 per cent. of sour milk starter.

In this way neutral citrates, acetates and phosphates are found, as can be predicted, to increase the final acidities, and so they are buffers. Casein, albumen,

peptone, and gelatin have buffer action, which is limited with the last mentioned (by solubility). Commercial pepsin, pancreatin and rennet extract are likewise buffers. By the action of pepsin on casein or albumen the buffer action of these can be made to equal, then exceed, that of Witte's peptone. Digestions with pancreatin reach a stage where the buffer action is diminishing. Lysine and asparagine gave negative results.

The addition of lactic acid before fermentation decreases the final acidities:

Lactic acid added, per cent.	0·00	0·04	0·08	0·13	0·17
Final acidity, per cent.	0·28	0·30	0·27	0·25	0·22

During a milk shortage reconstituted milk may be used for the fermentation, but this seldom ferments quite so well, and the addition of a little tri-sodium phosphate when dissolving the milk powder has been found useful.

The deposit which adheres to the pasteuriser (flash process) is rich in buffer substances, as the following figures (on the dry substance) show:

		I per cent.	II per cent.
Phosphoric acid (P ₂ O ₅)	..	33·2	20·0
Protein	7·6	44·8
Citric acid	1·0	—

Acid production and growth are closely correlated with lactic bacteria; hence the importance of buffers.

D. W. STEUART

THE LABORATORY
GAYMER & SON LTD.
ATTLEBOROUGH

SILICOSIS AND ITS INCIDENCE IN THE GOLD MINES

THE statement (ANALYST, 1934, 191) that the dust from the gold-bearing quartz rock of the Kolar Gold Fields, India, has not produced any cases of silicosis is not borne out by the facts. A committee was appointed in 1931 to investigate this question, and the conclusion was reached that silicosis does occur in these gold fields. Moreover, Dr. L. G. Irvine and Dr. S. W. Simpson, who were consulted, reported that "the pathological and radiographic evidence appeared to create a *prima-facie* case that instances of silicosis do occur among the underground workers in the Kolar Gold Mines," and many cases of the disease have been definitely diagnosed by pathologists.

It is said that silicosis does not develop in the Kolar Gold Fields until after 10 to 15 years' work underground. This may be due to the fact that the quartz reef in these Gold Fields contains only 8 to 17 per cent. of free silica, as compared with 80 to 90 per cent. in the South African rock. It is possible that acicular aggregates of sericite may be found in the matrix of the Kolar quartz pebbles, though this point has not yet been investigated.

Y. V. S. IYER

PUBLIC HEALTH INSTITUTE
BANGALORE (CITY)
INDIA

Official Appointment

THE Minister of Health has approved the following appointment:—

HUGH AMPHLETT WILLIAMS as a Public Analyst for the Metropolitan Borough of Shoreditch, in addition to H. G. Harrison (May 3rd, 1934).

Notes from the Reports of Public Analysts

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

JERSEY

REPORT OF THE STATES' ANALYST FOR THE YEAR 1933

THE total number of samples examined was 4381, as compared with 4017 in 1932, and 337 in 1884 (when the first Official Analyst to the States of Jersey was appointed). Of these, 3032 were samples of soils, fertilisers, etc., 434 were spirits, tobaccos, etc., for the Finance Committee, and 477 were foods, drugs and waters for the Sanitary Committee.

SOIL-TESTING AND ADVISORY SERVICE.—Jersey soil yields two crops per year. The soil-testing service guides the farmer as to the fertilisers he should use. Generally, special fertilisers are prescribed, based on the simple tests for reaction, a judgment of physical condition, the past history of the soil, and the requirements of the proposed crops. The rapid increase in the number of samples of soil submitted (from 135 in 1925 to 3008 in 1933) proves that the service has justified itself.

SPRAYS.—Eleven samples of commercial sprays were examined; they contained from 12·2 to 30·5 per cent. of copper. For the determination of the copper-content the volumetric iodide method of the A.O.A.C. is used. Also, both dry sprays and preparations for wet sprays are shaken with a large volume of water and allowed to stand; the presence of free copper in solution has been found to be connected with "scorching," and the greater the amount of acid required to produce soluble copper the slower appears to be the action of the spray.

OILS AND IMPORT DUTIES.—A sample of olive oil was found to be genuine, and a "salad oil" contained not less than 70 per cent. of arachis oil, which is dutiable when it is a Continental, not an Empire product.

JERSEY MILK AND BUTTER.—The 93 samples of milk examined contained an average of 4·94 per cent. of fat and 9·44 per cent. of solids-not-fat. No prosecutions were instituted, certain poor samples being found to be the result of incorrect treatment of the cow.

Thirty-eight samples of Jersey butter were of good quality. Monthly samples taken from two of the best-known local dairies showed an average Reichert-Meissl value of 29·8 (32·3 to 28·2), and an average Polenske value of 4·0 (4·9 to 3·2).

The importation of cows, heifers and bulls into Jersey has been prohibited since 1789 (except that for a few years foreign cattle were imported for meat and killed on the quay). This purity of strain is almost certainly unique in the civilised world, and the Jersey breed has been exported in very large numbers. The figures show the quality of milk and butter they produce in their native island.

CREAM.—Thirteen samples of fresh liquid Jersey cream contained from 65·8 to 45·1 per cent. of fat (average 53·6 per cent.).

CANNED LIQUID EGG.—A sample had been preserved by rendering it slightly acid, the user being instructed to neutralise the acid with sodium bicarbonate when the egg was required for use in cooking.

WATER SUPPLY.—Of 210 samples of well- and rain-water examined, 100 were satisfactorily free from pollution, but 16 of these were contaminated with lead. The Jersey waterworks supply is obtained from surface streams; there are three reservoirs of 90 million gallons capacity in all, sufficient for fifteen weeks of the peak summer demand. In addition to the slow sand-bed filters, two types of mechanical

pressure filters have been installed. The temporary hardness (as chalk) averages 1 part per 100,000, and coagulation of the aluminium sulphate is assisted by chalk or sodium aluminate, or both. Chloramine treatment has been used on the filtered water since 1930.

TESTS FOR TRACES OF CHLOROFORM.—A small bottle received from the police was empty, except for a little “dew” on one side. The bottle was suspected to have contained chloroform, and, on opening it, there was a strong smell of that drug. One ml. of alcohol was introduced into the bottle and shaken; on the resulting alcoholic solution reactions for chloroform were obtained by the carbylamine and Fujiwara’s pyridine tests; chlorine was obtained on hydrolysis; and by Moffitt’s modification of the Lustgarten test (ANALYST, 1933, 58, 2) 0.5 ml. of the alcoholic solution was found to contain 0.002 ml. of chloroform.

URINE.—A sample of “tea” from a workman’s can contained 1.5 per cent. of urea and 0.5 per cent. of chlorine (with uric acid, calcium oxalate crystals and granular casts), corresponding with approximately 50 per cent. of urine.

C. P. MONEY

COUNTY OF KENT

REPORT OF THE COUNTY ANALYST FOR THE FOURTH QUARTER, 1933

LOSSES IN MEAT DURING COOKING.—Four pieces of meat were placed in the same oven and cooked for fifty minutes, after which the gravy and fat produced from each piece of meat were poured off and collected separately. The percentage losses in fat, gravy, etc., from the four steaks were as follows:

Home-killed	15.9	Argentine frozen	33.0
New Zealand frozen	27.9	Argentine chilled	31.2

The loss of weight on cooking English-killed beef was, therefore, only one-half of that sustained by the others. The loss of weight with all the colonial meats was very considerable, and amounted to about one-third of the total weight of meat. The importance of these losses lies in the fact that they determine the size and weight of the meat placed before a consumer after cooking. Whereas the loss sustained on cooking 16 oz. of English meat amounted to about 2½ oz., the loss with frozen meat was about 5 oz. The loss on cooking was not due to the frozen meat containing large quantities of fat, because the home-killed meat contained more fat than two of the other meats examined.

The gravy and fat were collected from each piece of meat after cooking and the amounts of these are below expressed as percentages of the fresh meat:

	Home-killed	New Zealand frozen	Argentine frozen	Argentine chilled
Fat	0.4	6.7	5.0	1.8
Gravy	5.4	11.5	16.7	16.3

The composition of the gravies was in every instance similar. Owing, however, to the large volume of gravy lost from the frozen meats, the total loss of nutrient matter was much greater than from English meat. The loss of soluble mineral salts from frozen and chilled meat is very considerable, amounting to as much as 31 per cent., whereas for English meat the loss is only about 12 per cent. The results now obtained confirm others which I have obtained, and clearly indicate that less cooked meat is obtained from frozen and chilled beef than from English-killed beef. The loss on cooking includes not only water and fat, but also certain quantities of soluble protein and, possibly more important still, water-soluble mineral salts. These losses are very much less with home-killed beef.

F. W. F. ARNAUD

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.

MIDLINGS AND THE WHEAT ACT

R. AND W. PAUL, LTD. v. WHEAT COMMISSION

ON May 9th Mr. Justice Roche gave judgment in the action brought by Messrs. R. and W. Paul, Ltd., against the Wheat Commission, to obtain a decision whether, under the Wheat Act, 1932, wheat offals, known in the trade as "middlings," could be imported without liability to quota payment.

On various dates between April, 1933, and January, 1934, the plaintiffs had imported consignments of wheat offals, described as middlings, and, in particular, on October 24th, 1933, had received a parcel of middlings from Germany, and had paid an import duty on that parcel. Subsequently the Wheat Commission claimed quota payment on that parcel, but the plaintiffs contended that middlings were not liable to quota payments and refused to pay.

The Wheat Commission wished to have the question of the plaintiffs' liability settled by arbitration under a by-law, No. 20, of the Wheat By-Laws, 1932, made in pursuance of Sec. 5(1) and Sec. 5(2) (m) of the Wheat Act, 1932, but the plaintiffs contended that the by-law was invalid, and that they were not bound to submit to arbitration under by-law 20 on the question whether this consignment was liable to quota payment or was flour for the purposes of the Wheat Act, 1932. The plaintiffs also claimed the return of money which they had been obliged to pay in respect of other consignments of middlings from Germany.

The defendants contended that the by-law was valid, and that the Court had no jurisdiction to deal with the action. According to the definition in the Wheat Act, wheat offals are the residual products which, in the process of milling wheat, are extracted therefrom as germ or for animal or poultry food, and the defendants contended that nothing could be offal if it contained more than a normal quantity of material that could be extracted. With regard to the earlier consignments the defendants pleaded the Public Authorities Protection Act, alleging that the action had not been begun in time.

Sir Leslie Scott, K.C., and Mr. John Whyatt appeared for the plaintiffs; Sir William Jowitt, K.C., and Mr. Hubert Hull for the defendants.

Mr. Justice Roche decided that the Court had jurisdiction in the matter. The effect of by-law No. 20 of the Wheat By-laws, 1932, made in pursuance of sec. 5 of the Wheat Act, 1932, was, if valid, to obstruct all reference to the Courts. Mere authority to make by-laws at large was not authority to make by-laws of that nature. The Wheat Act did not authorise any such by-law as that.

His Lordship, in giving judgment, said that the real issue in the action was the construction of the statute. The parcels in question were said by the defendants to be the result of milling that was not in accordance with normal practice; therefore, it was said, that they were not offals and residuals within the definition of the Act, and therefore were flour.

The plaintiffs' contention was that those middlings were offals made as residual or by-products in the milling of flour; that they were substances extracted for animal or poultry food, and that they were therefore substances separated in the milling as wheat offals, and as such were expressly taken out of the category of flour, and did not attract quota payment. It was also said that, in so far as this might be material, fine or rich middlings, such as these, were produced before

and at the time when the Wheat Act came into force, and were residuals or offals, and were known and described as such.

He found on the facts that all the parcels were separated in the milling of the wheat for flour as the primary product, and that they were separated in the milling as wheat offals or residual products.

With regard to the construction of the statute, it was his opinion that if the substances were, in fact, offals or residuals, and were intended for animal or poultry food, they were exempt from quota payment. No definition of flour or reference of the separation of offals to a standard was to be found expressed in the Act, and to give effect to the Commission's contention would be to legislate and not to interpret. An effort had been made to base a difference on the fact that fine middlings might be separated and used as flour. He found that that contention failed. The real point was that the millers, in the process of milling, had separated the middlings in question as a residuary product. On these facts he found that the plaintiffs were entitled to succeed.

With regard to the first three parcels, he held that the defence of the Public Authorities Protection Act was good, and covered those items of the plaintiffs' claim.

Judgment was given for the plaintiffs for £1912 5s. 2d., with a declaration of non-liability for payment where such payments had not yet been made. Leave to appeal was granted.

Report of the Departmental Committee on the Composition and Description of Food

THE Committee re-appointed by the Minister of Health and the Secretary of State for Scotland, on July 24th, 1933, have issued their Report, dated March 20th, 1934.* The terms of reference were as follows:

"To consider whether it is desirable that the law relating to the composition and description of articles of food should be altered so as to enable definitions or standards to be prescribed, or declarations of composition to be required, for articles of food other than liquid milk; and, if so, to recommend what alterations of the law are required."

The meetings were not open to the public, but opportunity was given to representative organisations to appoint persons to attend meetings when evidence was being taken, and memoranda were also received from the associations and other organisations set out in Appendix I of the Report. A list of the witnesses who gave evidence before the Committee is given in Appendix II. The minutes of the evidence are not printed in the Report, but it is suggested that copies thereof should be available for inspection at the offices of the Minister of Health and the Department of Health for Scotland. The Report deals with the questions submitted, under the following headings:

I. EFFECT OF EVIDENCE.—It is stated that virtually all the witnesses agreed that modern statutes and orders regulating the composition of food have operated in the public interest, and that their enforcement has proved practicable.

II. EXISTING DEFINITIONS, ETC.—It is pointed out that the Minister of Agriculture has power to make regulations respecting what is to be regarded as the normal composition of milk, cream, butter, and cheese. Reference is also made

* Cmd. 4564. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. 1934, pp. 18. April, 1934. Price 3d. net.

to the arrangement between the Society of Public Analysts and the Food Manufacturers' Federation as to the composition and labelling of specified descriptions of jams, to the voluntary grading of a number of articles by manufacturers who elect to use a prescribed "grade designation," and to definitions and standards in use in the Dominions and foreign countries.

III. ADVANTAGES AND OBJECTIONS.—In the opinion of the Committee the effect of trade practice and competition on the character of certain articles indicates the desirability of having a power to fix definitions, but such power should be exercised in such a way as not to prevent reasonable development and improvement in the manufacture of an article. The objection that certain articles for which there is a demand might be driven off the market by the fixing of standards might be met by the sale of the sub-standard article under a name different from that of the standardised article.

The Committee have received no evidence that the lack of standards has resulted in malnutrition.

CONCLUSIONS AND RECOMMENDATIONS.

IV. THE MAIN QUESTION.—The Committee conclude that it is desirable that the law should be altered to enable definitions or standards to be prescribed or declarations of composition to be required, for articles of food other than liquid milk. The enabling power should be vested in the Minister of Health for England and in the Department of Health for Scotland (subsequently termed "the Minister" in the Report). In the opinion of the Committee, however, the case for the extension of standards or definitions to all articles of food has not been made out, although in some cases standards or definitions or declarations of composition are required for the protection of the consumers.

The Committee recommend that the power to fix standards should be used only where it is shown to be necessary for the protection of public health or the protection of the pocket of the consumer. Declarations of composition should be prescribed when it is desirable that the purchaser should be informed of some fact relating to either the composition or the preparation of the article. In any case, the power should only be exercised when the declaration can be checked by chemical analysis. The guiding consideration should be that, as far as possible, the same term should always mean the same thing.

Foods specially offered for infants and invalids should bear, on the label of the package containing them, a declaration of their contents.

Standards, declarations of composition, or definitions are not at present considered to be necessary for sweetmeats, unless it is found desirable to prohibit the use of certain ingredients.

It is suggested that the present limits or standards for arsenic, lead, tin, or other impurity, or for the addition to food of an ingredient claimed to be necessary (*e.g.* starch in shredded suet) should come under review.

V. ADVERTISEMENTS AND LABELS.—The Committee agree with the principle of the following recommendation, put forward by the Food Manufacturers' Federation, Patent and Proprietary Foods Section:—"It is our opinion that any attempt to control by statute statements about the composition of food will be stultified unless it is legally enacted that, for purposes of evidence as to the nature, quality and substance demanded of a food, specific claims made in advertisements shall be deemed to be part of the package label. Though it is theoretically true that the purchaser is expected to examine the label of a product before he completes its purchase, it is a matter of common knowledge that the vast majority of purchasers do not do so. The description on which they have been induced to buy the product is in a large number of cases only that contained in the advertisements, and we hold very strongly that progress in the standardisation and description of food will be seriously hampered until this matter is dealt with."

VI. WARRANTY.—The Committee consider that the retailer of a pre-packed article should be absolved from proceedings if he can show that he sold the article in the same condition as he received it, and had no reason to believe that it was not in accordance with legal requirements, and that he took all necessary precautions to protect it during storage.

The Committee also consider that the invoice referring to an article which may be the subject of a legal standard, and any label affixed to that article should be equivalent to a warranty that the article delivered may lawfully be sold under the name used.

Where samples of a pre-packed article on sale in the district of a Food and Drugs Authority are found to contravene legal requirements, action should be taken at premises where the article is packed.

VII. PROCEDURE FOR SETTLING STANDARDS AND DEFINITIONS.—The Committee do not recommend the constitution of a new permanent Advisory Committee, such as that advocated by the Society of Public Analysts and others. For articles in regard to which there should be no difficulty in arriving at a large measure of agreement with manufacturers and other interested parties the Minister, with the aid of his own experts, should consult any Government Departments concerned and confer informally with the manufacturers and others interested. Where there is a wide divergence of view between the parties interested it is recommended that the matter should be referred to a Committee of three independent persons who would hear evidence and report to the Minister. After receiving and considering the report it would be for the Minister to decide whether or not to proceed with the making of the Order.

Steps would have to be taken to prevent the importation of articles which contravened any standards or other requirements which had been laid down.

VIII. EXPENSES OF ADMINISTRATION.—The Committee are of opinion that alterations in the expenditure of Local Authorities resulting from the fixing of standards or definitions would not be material. They consider that the cost of administration would be materially reduced if the present law were amended by enacting that it shall not be essential to submit to chemical analysis an article of food, the nature or composition of which could be sufficiently proved in some other way.

IX. REVISION AND CONSOLIDATION OF STATUTE LAW.—It is generally agreed that the objects of the ancient statutes of pre-Victorian times dealing with the composition of tea and coffee are completely provided for by later legislation. The Committee therefore recommend that these Acts be repealed. Consideration should also be given to the question of replacing the two Acts of 1822 and 1836 (dealing with the composition of bread and flour) by new legislation more suited to present-day conditions. In the opinion of the Committee the time is ripe for the consolidation of the statutes dealing with the composition of food.

Report of the Committee on Trade Marks

THE Report of the Departmental Committee on the law and practice relating to trade marks was published on April 28th.*

The recommendations of the Committee include several that would involve fundamental changes in the existing law. Thus, it is recommended that a trade mark should be validly assignable for a part only of the goods for which it is registered, provided that such assignment is not likely to deceive or cause confusion.

Provisions should also be made for the registration, under proper safeguards, of persons authorised by a proprietor to use his registered trade mark. Provision should be made for the extended or defensive registration of a well-known registered trade mark, consisting of an invented word or words, which has become identified with the proprietor to such an extent that the use of the mark by others on goods other than those for which the mark is registered would create the impression that there was a connection between those goods and the proprietor of the mark.

A further recommendation is that the principle of the existing common law rule, whereby a word which is or has become the name by which an article is commonly known, is not protectable as a trade mark should be modified; and that Sec. 6(1) of the Trade Marks Act, 1919, should be amended so as to allow the proprietor of a word trade mark in respect of a patented article or substance to preserve his exclusive rights in the mark, if after a period of two years he can show that his trade mark is not the only practicable name or description of such article or substance.

The extension in certain directions of the legal rights of the proprietor of a validly registered trade mark is also recommended; in particular, the proprietor should be empowered to prohibit in relation to his trade mark certain acts which might injure the reputation or impair the value of his mark.

Definition of "Trade Mark."—The Committee propose that a "trade mark" other than a "certification trade mark" shall mean a mark used or proposed to be used by the proprietor upon or in physical or other relation to goods, for the purpose of indicating or so as to indicate a connection in the course of trade between the proprietor of the mark and the goods.

It is recommended that the operation of sec. 62 of the Trade Marks Act, 1905, should be limited to the registration in Part A of distinctive marks to non-trading bodies, and that such marks should, where practicable, be identified in use as certification marks. (Cf. ANALYST, 1933, 58, 473.)

* Cmd. 4568. H.M. Stationery Office, 1934. Price 1s. 6d.

Department of Scientific and Industrial Research

REPORT FOR THE YEAR 1932-33*

As in the previous year (*ANALYST*, 1933, 58, 227), the Report is divided into five sections, comprising the Report of the Commission of the Privy Council for Scientific and Industrial Research (pp. 1-5); that of the Advisory Council (pp. 6-22); a Summary of Work (pp. 23-83); Research Associations (pp. 85-128); and 7 Appendices (pp. 130-179).

The Report of the Advisory Council deals at considerable length with the scheme started during the war to encourage the establishment by industry of research associations. The grant in aid of one million pounds voted by Parliament in 1917 is exhausted, and a general review of the position is made. The conclusion is reached that such research associations have proved their potentialities to an extent that warrants substantial development, and the urgent financial needs of the situation are emphasised. During the year under review the duty of directing and supervising the conduct of Road Research has been transferred to the Department, and a preliminary programme of research is being considered.

NATIONAL PHYSICAL LABORATORY.—The annual report of the Laboratory for the year has been published (*ANALYST*, 1933, 58, 402). Since the Eighth General (International) Conference of Weights and Measures had various questions of international standardisation to discuss, the work of the National Physical Laboratory was brought to definite stages in anticipation. The results of the preliminary determination of the length of the metre in terms of the wave-length of the red radiation from cadmium have been published (J. E. Sears and H. Barrell, *Trans. Roy. Soc.*, 1932, A, 231, 75), together with a description of the wave-length comparator, and the final determinations of the yard and the metre in air and *in vacuo*, in terms of light waves, and of the refractive index of air, have been completed and will be published shortly. A comparison of various sources of radiation for use with the comparator has also been made (J. E. Sears and H. Barrell, *Proc. Roy. Soc.*, 1933, A, 139, 202). The results of the determination of the absolute unit of electric current by means of the ampere balance are now available, and it is found that the absolute ampere is greater than the international ampere by 12 parts in 100,000, the ratio being subject to a maximum uncertainty of 4 parts in 100,000. An inter-comparison of thermo-couples has been carried out by the Bureau of Standards, the Reichsanstalt and the National Physical Laboratory, and the scales have been brought into agreement within 0.1°C. at all points of the range 660°C. to 1063°C. Preliminary results on the use of a black-body radiator at the freezing-point of platinum as a primary standard of light show that agreement with the Bureau of Standards will be attained.

The Metrology Department have carried out the statutory decennial inter-comparisons of the Imperial and Parliamentary standards of length and weight. The comparison of the yard and metre standards is practically complete, and the new vacuum balance is being used for the comparison of the pound and kilogramme. The investigations on the thermal and electrical conductivities of heat-resistant alloys have shown that the thermal conductivities of the alloys examined tend towards a common value in the neighbourhood of 1000°C.

FUEL RESEARCH.—The Report for the year ending March, 1933, has been published (*ANALYST*, 1934, 34). Reference is made to the methods for the quantitative determination of coal ash (*ANALYST*, 1933, 58, 614).

FOOD INVESTIGATION.—The Report for 1932 has been published (*ANALYST*, 1933, 58, 611). Work on the metabolism of carbohydrates in fish has shown that

* Obtainable at Adastral House, Kingsway, W.C.2. Price 3s. net.

in the haddock's liver glycogen decreases rapidly and disappears in 60 hours, whilst free sugar accumulates slowly and continues to do so after the complete disappearance of the glycogen; finally, after 150 hours, it reaches a maximum value corresponding with the loss of glycogen. A very small accumulation of lactic acid occurs over the whole period. The results of a detailed study of the quantitative variations in vitamin *A* of halibut liver oil are to be published. In addition to work already published on the metabolism of fat in fishes (*Biochem. J.*, 1932, **26**, 1978 and 1985), the fat of the salmon, as smolt, the porpoise, and, at the other end of the scale, the fats of certain members of the zöo-plankton, and of various algae are being investigated.

The Ditton Laboratory is making a second series of experiments on the gas-storage of the following varieties of apples:—Monarch, Blenheim Orange, Worcester Pearmain, and Cox's Orange Pippin.

BUILDING RESEARCH.—Weathering measurements of atmospheric pollution are being tested in conjunction with Atmospheric Pollution Research Committee (ANALYST, 1934, 280). Progress has been made in the study of the physical factors influencing weathering, in the development of freezing and crystallisation tests and the correlation of their results with the behaviour of bricks, stone, etc., in structures, and with the exposure tests and stone preservative experiments. In the work on asphalts and bitumens good results have been attained with bitumen applied hot as an adhesive for bonding rubber flooring to concrete.

FOREST PRODUCTS RESEARCH.—The Report for the year has been published (ANALYST, 1933, **58**, 155). Work on the utilisation of thinnings from Forestry Commission and other plantations for telegraph and transmission poles has been in progress, particularly as regards their mechanical and physical properties and capability of absorbing creosote. The liability of timber to *Lyctus* infestation has been found to depend upon the relation between pore diameter and diameter of the ovipositor of the beetle.

METALLURGICAL RESEARCH.—Work on the removal of gases from light alloys has shown that there is on any exposed surface of molten aluminium an oxide skin which is highly impervious to gases, and to achieve the rapid elimination of gases the character of this skin must be altered. The nitrogen used to dilute the halide removes the liberated gas, and it is suggested that treatment with a mixture of raw cylinder nitrogen and carbon tetrachloride might be suitable in commercial practice. Further study of aluminium alloys capable of age hardening, and of the X-ray analysis of single crystals of high purity alloys is in hand.

WATER POLLUTION RESEARCH.—(See ANALYST, 1934, 282.)

CHEMICAL RESEARCH.—It is noted that some 38 British chemical firms and other outside organisations have applied to the Laboratory for advice and information. Two series of organic arsenicals have been investigated in the search for drugs to combat African sleeping sickness: derivatives of fluorenone and fluorenol containing arsenical groupings, and derivatives of *p*-arsanilic acid having the general formula $\text{AsO}_3\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}(\text{CH}_2)_n\cdot\text{CO}\cdot\text{NRR}'$.

ILLUMINATION RESEARCH.—The results of the investigation to discover the most suitable traffic signals have been embodied in a British standard specification. The investigation of the fundamental properties of diffusing glass-ware for the British Standards Institution has been continued.

RESEARCH ASSOCIATIONS

Only a few activities of a small number of these can be mentioned.

WOOL INDUSTRIES RESEARCH ASSOCIATION.—In both the woollen and worsted processes a method has been evolved whereby the fibres are treated in bulk to render them unshrinkable.

Ionised Oil for Wool Textiles.—A new type of oil known as ionised oil has been developed for wool textile purposes. This has been specially treated electrically, so as to be non-oxidisable, water-miscible, and to possess bleaching properties. The oil has now been in factory use for over a year, and thousands of yards of cloth, especially of the grey flannel type, have been processed with ionised oil, and put on the market.

Standardisation of Fastness of Fabrics.—The work carried on by the Society of Dyers and Colourists for the standardisation of fastness of dyed fabrics to various ordinary agencies has resulted in the selection of standard fabrics representative of 8 different degrees of fading, in red and in blue. Since wool dyestuffs usually are less susceptible to atmospheric fading, they have been used on a wool base. A series of standard tests expressing the degree of durability of standard fabrics has been drawn up.

LINEN INDUSTRY RESEARCH ASSOCIATION.—*Effect of Dyes on Tendering.*—It has been shown that when linen dyed with a range of vat and insoluble azo dyes is exposed in the open, excessive tendering occurs with a number of orange and yellow vat dyes. Some of the dyes examined, including several insoluble azo combinations, exert a protective effect under the same conditions.

The behaviour of cotton yarn dyed with a number of vat and insoluble azo dyes and woven as strips into linen glass cloths has been examined during a variety of laundry treatments. Some yellow and orange vat dyes have been shown to produce undue tendering when the material is exposed in the open between successive laundry treatments.

THE BRITISH FOOD MANUFACTURERS' RESEARCH ASSOCIATION.—*Research on Sterilisation.*—In the investigation of sterilisation problems of meat products, a report has been issued to members on the determination of the rate at which the heat used penetrates different types of products and sizes of packages. The temperature and time of heating required to destroy a particular type of bacterium which gave rise to serious trouble in several factories were investigated, and, although the spores were as resistant to heat as any so far recorded (standing boiling for over 7 hours, and surviving half an hour's heating to 230° F.), it was found not to be pathogenic, and its growth was inhibited by percentages of salt above a certain limit. Also, the older spores were found less resistant than the younger.

The reaction of certain types of bacteria to pickles of different strengths is being studied. One type will cause souring in bacon if the cure has been too mild, and the strength of salt that will inhibit growth is being sought. Results on the effect of salt on the growth of *B. coli communis* indicate that it is highly improbable that any of the bacteria usually associated with food poisoning outbreaks can survive the curing in a reasonably strong pickle.

D. G. H.

Addition to the Poisons Schedule

DINITRO PHENOL; DINITRO CRESOL

At a meeting of the Privy Council on April 11th the following resolution was received from the Council of the Pharmaceutical Society, acting in exercise of the powers vested in them by the Pharmacy Act, 1868, as amended by the Poisons and Pharmacy Act, 1908:

“That by virtue and in exercise of the powers vested in the Council of the Pharmaceutical Society of Great Britain, the said Council doth hereby resolve and declare that the Schedule to the Poisons and Pharmacy Act, 1908, ought to be amended by the addition to Part I of the following words:

Dinitro phenols; dinitro cresols; preparations or admixtures containing dinitro phenols; preparations or admixtures containing dinitro cresols.”

The said Society, having submitted their resolution for the approval of the Privy Council, the Lords of the Privy Council signified their approval of the said resolution. (See *London Gazette*, April 13th, 1934.)

International Atomic Weights

FOURTH REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS OF THE INTERNATIONAL UNION OF CHEMISTRY*

THE report covers the 12 months ending September 30th, 1933. The atomic weight of carbon has been shown once more to be slightly higher than the official value 12.00, but no change is being made for the present. The eight following elements appear in the 1934 Table with modified atomic weights: (i) The atomic weight of potassium is now 39.096, as the result of numerous analyses of the chloride and bromide. (ii) The value for arsenic is slightly reduced to 74.91; as in the case of potassium this number was obtained by comparison with silver, arsenic trichloride and tribromide being used. (iii) Selenium was made to act on weighed quantities of the purest silver; the weight of the synthetic silver selenide led to the lower atomic weight 78.96, which has been adopted. (iv) Indium trichloride and tribromide were analysed, the atomic weight of indium being calculated at 114.76. (v) Tellurium was converted into tetrabromide, and this in turn into silver bromide. The higher figure, 127.61, is the mean of closely agreeing results obtained by the above method and the synthesis of silver telluride. (vi) Caesium chloride, spectroscopically free from rubidium and potassium, was converted into silver chloride; the value 132.91 is now adopted. (vii) Ytterbium chloride, purified by Prandtl and tested by X-ray analysis, was compared with silver; the atomic weight of ytterbium is now lowered to 173.04. (viii) Osmium, prepared from the re-distilled tetroxide, was re-oxidised, and the tetroxide was converted into ammonium chloro- and bromo-osmate. The pure dry salts were reduced in hydrogen, which was replaced by nitrogen before exposure of the metal to the air. The higher figure, 191.5, has been inserted in the Table.

Lead.—A number of careful determinations of the atomic weight of lead from various sources gave the following results:—Common lead, 207.211; from cyrtolite (New York State), 205.927; from Katanga pitchblende, 205.97; from Morogoro uraninite, 206.038; from Katanga curite, 206.031. The method adopted was conversion of lead chloride into the silver compound. W. R. S.

* By G. P. Baxter (chairman), Mme Curie, O. Hönlgschmid, P. Lebeau, and R. J. Meyer. Union Internationale de Chimie, Secrétariat Général: 49, Rue des Mathurins, Paris.

Third International Technical and Chemical Congress of the Agricultural Industries

THIS Congress was held in Paris, from March 26th to March 31st, 1934, under the auspices of the French Ministry of Agriculture. Senator Fernand David, Member of the National Agricultural Academy of France, was President of the Congress, and Professor Joseph Pérard was President of the Executive Committee of the Congress. The social events included a reception, by the President of the Republic, of the foreign delegates to the Commission.

The set subjects down for discussion at the Congress were divided into the following five groups:—

GROUP I. SCIENTIFIC AND ECONOMIC QUESTIONS.—These included: (i) Determination of p_H and its value in the agricultural industries, (ii) Waste liquors, (iii) Utilisation of over-production of agricultural products, (iv) Improvement of the sugar beet and cane by genetic selection.

GROUP II. SUGAR.—Subjects considered were: (v) Purification of sugar juices, (vi) Crystallisation of sugar, (vii) Storage of sugar.

GROUP III. FERMENTATION INDUSTRIES.—The questions discussed were: (viii) Fermentation—in both its theoretical and practical aspects, (ix) Continuous diffusion, (x) The fruit juice industry.

GROUP IV. FOOD INDUSTRIES, including: (xi) Qualities demanded in bread in different countries and the corresponding properties of flours and wheats, (xii) Evolution of plant used in the vegetable oil industries, (xiii) Use of vegetable oils in motors, (xiv) Collection, transport and treatment of milk, (xv) Cocoa and chocolate.

GROUP V. ALLIED INDUSTRIES.—(xvi) Technique and economics of alcohol fuels and their use in different countries, (xvii) Wood distillation.

In addition to communications on the above subjects, papers dealing with analytical, technical and economic matters were read before the different sections.

It was decided that the next Congress be held in 1935 in Brussels, where there will be an Exhibition during that year, and that subsequent Congresses shall take place at intervals of three years.

The Society of Public Analysts and other Analytical Chemists was represented at the Congress by Mr. T. H. Pope.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Determination of Hydroquinone, especially in Salt Herrings.
W. Preiss. (*Z. Unters. Lebensm.*, 1934, **67**, 144–160.)—In the iodimetric determination of hydroquinone in small amounts, the use of potassium bicarbonate to render the solution alkaline causes inaccuracy, unless the liquid is previously saturated with carbon dioxide. Preferable is the use of either disodium phosphate or sodium acetate. Contrary to statements in the literature, quinone may be distilled unchanged in steam, provided that the solution is kept at a definite p_H value. Hydroquinone is now added to salt herrings to delay their alteration,

and the following methods have been elaborated to detect and determine this substance in the pickling brine and in the fish.

If hydroquinone has been used, the separated brine shows very little fat and has a deep-red colour, even when all the hydroquinone has undergone change.

About 150 grms. of the well-mixed brine are weighed—soon after the separation—in a 200-ml. flask, and 15 ml. each of about 30 per cent. acetic acid solution, 5 per cent. potassium ferrocyanide solution and 10 per cent. zinc sulphate solution are added. The liquid is made up to 200 ml. with water, well shaken, and, after a time, filtered through a dry filter into a dry vessel, the first few ml. of the filtrate being discarded. When a little of the liquid (A) is poured down the wall of a test-tube containing a solution of silver nitrate in excess of ammonia solution, the zone of separation becomes red or violet-red if small amounts of hydroquinone are present; with larger amounts (a few mgrms.), a brownish-black precipitate appears on mixing the two layers. If quinone is present, addition to the filtrate of an acidified potassium iodide solution containing starch produces at once a blue colour.

To determine hydroquinone in the brine, 100 ml. of the clear filtrate (A) are placed in a distilling flask with 3 ml. of 5 per cent. sulphuric acid, 5 ml. of glacial acetic acid, 40 grms. of sodium chloride, and 10 ml. of ferric chloride solution (about 30 per cent.). The condenser-tube is fitted with an adapter dipping into a Sendtner flask (as used for the determination of iodine value) containing about 5 ml. of 0.1 *N* sulphuric acid and 15 ml. of water. The distillation is carried out in a current of steam, and is continued until all the quinone has passed over, the collection of 100 to 150 ml. of distillate usually sufficing. The distillate is treated with about 1 to 1.5 gm. of potassium iodide and 5 to 10 ml. of dilute sulphuric acid and, after standing for a short time in the closed flask, is titrated with 0.02 *N* sodium thiosulphate solution, starch being added towards the end of the titration. Multiplication by 1.145 of the number of ml. of the thiosulphate used gives mgrms. of hydroquinone in the filtrate used; this factor allows for the fact that only 96 per cent. of the total hydroquinone is recovered by the above procedure. Excessive frothing during the distillation may be overcome by passing carbon dioxide through a tube ending just below the neck of the distilling flask.

The presence of hydroquinone and quinone in the herrings themselves may be detected by subjecting a cold absolute alcohol extract of the herrings to the reactions used for the brine. In no case has quinone been found in herrings salted with a mixture of hydroquinone and rock-salt. To determine the hydroquinone, 100 grms. of the minced and mixed herrings are ground in a glazed mortar with 150 grms. of anhydrous sodium sulphate. The mixture, together with exactly 200 grms. of absolute alcohol, is transferred to a 500-ml. Sendtner flask, which is vigorously shaken at short intervals during 1 to 1½ hour. The mass is then filtered through a dry pleated filter into a weighed flask, and the whole of the clear filtrate (120 to 140 grms.) is transferred to a distilling flask with the aid of a little alcohol, treated with 0.5 to 1 ml. of 5 per cent. sulphuric acid, and distilled from a boiling water-bath and in a current of carbon dioxide until 15 or 20 ml. remain. This is allowed to cool somewhat in the gas stream, and is then treated with 5 ml. of glacial acetic acid, 50 grms. of sodium chloride, 7 to 8 ml. of about 30 per

cent. ferric chloride solution and sufficient water to bring the volume up to 150 or 200 ml. The subsequent procedure is as described above for the determination of hydroquinone in the brine. The sample of herrings to be examined should be taken from the brine-covered lower layers of the cask, and the extraction with alcohol should be carried out as soon as possible after the sampling. During storage of the herrings, their content of hydroquinone diminishes owing to oxidation to quinone and interaction of this with the constituents of the herrings. T. H. P.

Phosphatids of Wheat Flour. F. E. Nottbohm and F. Mayer. (*Z. Unters. Lebensm.*, 1934, **67**, 369-379.)—The authors have found previously (*ibid.*, 1933, **65**, 55) that only one-half as much choline is obtainable from cocoa beans by direct extraction with alcohol as by the magnesia process, which is now modified as follows to apply to material rich in starch:—Ten grms. of the material (flour) are thoroughly ground with 2 grms. of calcined magnesia, and the whole is mixed with a little water to give a uniform paste. This is washed into a 300-ml. Erlenmeyer flask to a total volume of about 150 ml., and is heated for an hour in a briskly-boiling water-bath. The swollen mass is cooled, transferred to the mortar originally used, and mixed gradually with alcohol, 150 ml. of which are added in all. The clear supernatant liquid is poured off, and the precipitate is centrifuged to recover the rest of the alcoholic solution. The solid residue still retains about 5 per cent. of the total choline, which may be extracted by repeating the treatment with magnesia and alcohol. The combined alcoholic extracts are evaporated to about 50 ml. with hydrochloric acid and are prepared for the determination of the choline by heating in an autoclave (*ANALYST*, 1932, **57**, Abst., 322).

Examination in this way of the various constituents of wheat flour shows that the gluten contains little choline and the wash-water rather more, the main quantity being in the starch washed away. The choline is present in the flour, not as free base, but as choline-lecithin. The wheat phosphatid has the P : L number (*ANALYST*, 1934, Abst., 182) 1.56, and contains about 26 per cent. of carbohydrate, calculated as glucose, but the starch washed out from the flour appears to be free from carbohydrate. The amount of phosphatid found in wheat flour is about three times that formerly assumed, and the proportion in bran is still greater. Trigonelline is not present either in flour or in bran. T. H. P.

Investigation of Peas. R. Nesen. (*Z. Unters. Lebensm.*, 1934, **67**, 195-197.)—A number of samples of peas, both in the pod and shelled, were examined. Most of the samples failed to comply with the requirements of the *Codex alimentarius austriacus* with regard to colour, odour, regularity, freedom from borers, age, and impurities (cankered, broken or immature peas, foreign seeds, insects, straw, soil, stones, etc.). Both yellow and green peas in the pod showed higher percentages of altered seeds than the shelled wares, but these contained the higher proportions of partly eaten and broken peas. Examination in ultra-violet light revealed, with many of the samples, the presence of points or spots either black or showing intense sulphur-yellow fluorescence; these points or spots are produced by either bacteria or moulds and indicate damp storage. T. H. P.

Changes in the Composition of the Potato during Winter Storage. L. Erdős. (*Z. Unters. Lebensm.*, 1934, **67**, 198–202.)—A number of kinds of potatoes, specially suitable for growing in the dry climate of Hungary, were examined in December, 1931, and, after storage in a cool, dry place, in April and June, 1932. During the storage, the specific gravity mostly increased steadily, the extent of the increase varying with the kind. With some sorts the specific gravity was lower in June than in April, the loss of moisture and dry matter being unaccompanied by the shrinking which usually occurs. In relation to the dry matter, the ash increases during storage, and the protein increases both in the tuber and in the germ. Neither the starch-content nor the proportion of dry matter runs parallel with the specific gravity, and Maercker's table for determining starch or dry matter should be used only when results are required quickly, and then only for ripe potatoes. Far more accurate results are furnished by the protein- and salt-free extractives, which contain little but the starch. T. H. P.

Iodine-Content of Pennsylvania Potatoes. D. E. H. Frear. (*J. Agric. Res.*, 1934, **48**, 171–182.)—The iodine in 135 samples of potatoes from different parts of Pennsylvania was determined by means of a modification of the closed combustion method of Karns (*Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 299, 375), in which carbon dioxide gas was used, and the absorption vessel consisted of a Witt filtering apparatus, with three thicknesses of filter-paper or paper towelling within the ground-glass joint sufficiently porous to allow the passage of the gases, but condensing and retaining the iodine. The minimum iodine-content was 10 parts, the maximum 216 parts, and the mean 77.8 parts per billion, expressed on a moisture-free basis. The mean iodine-content of potatoes grown in the north-central part of the State was considerably lower than that for the other localities, but, although potatoes grown on glaciated soils contained slightly more iodine than those from non-glaciated soils, no significant differences could be correlated with type of soil; nor did the use of fertilisers affect the iodine-content. Two samples from a marine soil, however, had a high iodine-content. No correlation was found between the size or variety of potato and iodine-content, nor could incidence of goitre be related in any way to the proportion of iodine. D. G. H.

Merck's Diastase, a Proposal for Barley Analysis. W. Piratzky. (*J. Inst. Brewing*, 1934, **40**, 175–176; *Woch. Brau.*, 1934, **51**, 33–34.)—Merck's new "Diastase reinst, Art. No. 3029" is suggested as preferable to a freshly-prepared malt-extract for standardisation of the method of digesting and saccharifying barley. It is stated to be prepared by precipitation with absolute alcohol of extracts of malt in dilute alcohol, and it contains water, 9 to 10 per cent.; ash, 10.4; nitrogen, 7.75 (corresponding with 48.4 per cent. of protein); and sugar (as maltose), 25.5 per cent.; the remaining 15.7 per cent., presumably, represents dextrans, and there is a small quantity of flocculent matter insoluble in water, due probably to protein denatured by drying. The diastatic activity is 10 times that of a pale malt, and 100 ml. of a 1.3 per cent. solution are sufficient for a determination of the extract in barley, and give results in close agreement with those obtained by means of the usual malt extracts. Solutions of this strength show a loss in

activity of only 2 per cent. after 2 months in an ice-chamber if stored in sterile 100-ml. bottles, each containing a few drops of a mixture of 1 part of chloroform with 2 parts of acetone.

J. G.

Determination of Carbon Dioxide in Beer. **J. L. Baker and H. F. E. Hulton.** (*J. Inst. Brewing*, 1934, **40**, 171-173.)—The method, which is more suitable for routine purposes than the gasometric procedure previously described (*ibid.*, 1923, **29**, 427), but is not applicable to black beers, depends on the addition of known volumes of boiled and unboiled beer to an excess of a standardised (approximately 0.2 *N*) solution of barium hydroxide. Since boiling removes carbon dioxide, the difference between the back-titrations with 0.5 *N* oxalic acid is a measure of the carbon dioxide content (1 ml. of oxalic acid = 0.011 grm. of CO₂). Exactly 50 ml. of the baryta solution are measured into a flask with a long neck near the middle of which is a 70 ml. mark, with graduations at 0.5-ml. intervals above and below this, and about 20 ml. of the beer are then cautiously run in through a tube which reaches to the bottom of the bottle, the exact volume added being determined from the graduations on the neck. The mixture is washed into a flask with cold distilled water, and is titrated in the presence of 20 ml. of approximately 1.0 *N* barium chloride solution with the oxalic acid, phenolphthalein being used as indicator and the mixture being well shaken and kept cooled before and during the operation. Another 20-ml. portion of the beer is then well roused and boiled with 50 ml. of water until all carbon dioxide is expelled, a reflux condenser being necessary if the acidity (as acetic acid) exceeds 0.1 per cent., in order to avoid loss of acid; the solution is then cooled, and the baryta equivalent of the sulphates and phosphates in the beer is determined by repetition of the above titration. If the errors in the measurement of the volume of beer and in the titration are 0.1 and 0.2 to 0.3 ml., respectively, the error in the volume of carbon dioxide may attain 50 ml. per litre, or about 2.6 per cent. of the total volume; this is considered sufficiently accurate for routine work, and compares favourably with the accuracy obtained by removing the gas by boiling and weighing it after absorption in soda-lime. If the beer is in a pressure-tank, it must be transferred without loss of gas to a half-pint bottle fitted with a metal screw-stopper carrying two tubes, each provided with a valve (*e.g.* a motor-car petrol cock); one reaches nearly to the bottom of the bottle, whilst the other is shorter and projects just inside the stopper. The bottle is cooled in ice, the former (longer) tube is connected with the tap on the tank which is then opened, the valve on the longer tube then being also opened so that beer and froth partly fill the bottle. The second valve is then opened slightly so that the beer escapes slowly, and after 10 minutes under these conditions both cocks are closed again. If the beer is already in bottle, a similar procedure may be used to transfer it to the measuring flask, the bottle being clamped in an inverted position and fitted with a rubber stopper carrying two glass tubes, each provided with a pinch-cock.

J. G.

Frozen Wine. **A. Heiduschka and C. Pyriki.** (*Chem.-Ztg.*, 1934, **58**, 229.)—A process for the treatment of fruit wine on the large scale involves the freezing of the wine and separation of the solid and liquid portions by means of a centrifuge (see D.R.P., 163,101, 23rd Nov. 1902). In the present experiments

the wine was immersed in a mixture of ice and salt until it became pasty, and was filtered on a cooled funnel; the first runnings were then frozen and re-filtered. The analyses are given below, columns (a) and (b) referring to a German white and red wine, respectively. They show, on the whole, that the constituents of the wine tend to accumulate in the unfrozen portions (*cf.* O. Reinke, *ibid.*, 1934, 58, 17; and P. Walden, *ibid.*, 1934, 58, 96). The taste of these portions had deteriorated, and the bouquet was lost.

Constituent	Liquid portion (grms. per litre)						Thawed expressed residue (grms. per litre)			
	Original wine (grms. per litre)		First		Second		First		Second	
	a	b	a	b	a	b	a	b	a	b
Sp.gr. at 4° C. ..	0.9934	0.9955	0.9924	0.9956	0.9913	0.9954	0.9946	0.9960	0.9937	0.9962
Alcohol	77.00	84.60	101.10	99.70	113.10	116.10	59.10	66.90	77.00	72.90
Extract	18.20	26.20	24.40	32.50	28.10	37.60	14.40	21.60	19.00	24.20
Ash	1.85	2.95	2.45	3.70	2.50	4.57	1.44	2.58	1.85	3.05
Total acids ..	7.24	7.12	9.37	8.66	10.57	10.20	5.77	5.89	7.50	6.32
Volatile acids..	0.67	1.28	0.70	1.44	0.76	1.47	0.39	0.86	0.69	1.02
Titrated non-volatile acids	6.41	5.52	8.49	6.86	9.62	8.36	5.28	4.81	6.64	5.04
Lactic acid ..	3.82	2.80	5.04	3.17	5.59	3.95	3.36	2.24	3.95	2.64
Tartaric acid..	2.33	1.99	3.11	2.39	3.22	2.97	1.69	1.50	2.40	1.50
PO ₄ '''	0.25	0.26	0.29	0.30	0.34	0.36	0.18	0.20	0.23	0.25
Sugar	1.29	2.49	1.60	3.08	1.81	3.64	1.02	2.24	1.38	2.38
Glycerol	4.91	6.85	6.86	7.78	8.98	8.47	4.03	5.87	5.80	6.74

J. G.

Reif's Colour Reaction for the Detection of Benzylidenesorbitol.
H. Kreipe. (*Z. Unters. Lebensm.*, 1934, 67, 426-428).—This reaction (ANALYST, 1934, Abst., 44) may be relied on to detect sorbitol in wine or wine vinegar, provided that special attention is paid to certain details of the procedure. The benzylidenesorbitol to which the colour-test is applied must be as pure as possible. Even traces either of the yeast used to ferment the residual sugars of the wine or of the decolorising charcoal employed exert a disturbing effect on the colour reaction. The charcoal is best removed by filtration through a layer of Seitz filtering-material on a porcelain thimble. Purification of the precipitated benzylidenesorbitol by means of petroleum spirit, either alone or mixed with alcohol, must result in the removal of all traces of benzaldehyde. To exclude the possibility of benzylidenemannitol taking part in the colour reaction, A.R. sulphuric acid of sp.gr. 1.84 should be used, and care must be taken that none of this acid adheres to the wall of the test-tube. Drying of the precipitate at 75° to 80° C. must not be omitted, since a trace of residual moisture would alter the concentration of the acid, and consequently the solubilities of the benzylidene derivatives. Colour reactions, being subjective, are not suitable for forensic purposes, and the preparation of hexa-acetylsorbitol (*cf.* Jahr, ANALYST, 1930, 55, Abst., 452), which can be exhibited, is then of advantage in proving the presence of sorbitol in a wine or wine vinegar.
T. H. P.

Composition of Oil of Carrots. L. Palfray and (Mlle) A. M. Lapesqueur. (*Compt. rend.*, 1934, 198, 1365-1367).—This oil, obtained by steam distillation, is free from methoxy and ethoxy groups and nitrogen, and contains at most traces of phenols. It shows no fluorescence in ultra-violet light, fixes bromine in

chloroform solution, and gives a yellow colour with antimony trichloride (*cf.* Sabetay, *ANALYST*, 1933, **58**, Abst., 712). The constants are: Sp.gr. 0.9413 at 17°/4° C., $n_D^{18.5}$ 1.4931 (α_D^{17} + 3.90°, acid value 3.47, saponification value 19.73, or, after acetylation, 55.5. The oil combines to a small extent with sodium bisulphite, but no definite oxime or semicarbazone could be isolated. The free acids present comprise formic and acetic acids. Other constituents detected were (1) *l*-pinene, and (2) an unsaturated compound, C₁₅H₂₆O, apparently identical with Asahina and Tsukamoto's carotol (*J. Pharm. Soc. Japan*, 1925, [525], 1), which fixes one molecule of hydrogen in presence of oxidised platinum and appears to contain one hydroxyl group.

T. H. P.

Determination of Chlorogenic Acid in Coffee. C. Griebel. (*Z. Unters. Lebensm.*, 1934, **67**, 452-456.)—Hoepfner's statement that treatment of coffee with steam prior to roasting diminishes the content of chlorogenic acid (*ANALYST*, 1933, **58**, Abst., 100, 702; Plücker and Keilholz, *ANALYST*, 1933, **58**, Abst., 701; and *Chem.-Ztg.*, 1933, **57**, 875) is further discussed (*ANALYST*, 1933, **58**, Abst., 621). Roasting diminishes the content of chlorogenic acid of coffee by an amount depending on the degree of roasting. If Hoepfner's statement is correct, steam-treated coffees should show, after roasting, lower proportions of this acid than ordinary roasted coffees; this is, however, usually not so. The slight differences in this direction sometimes observed may well have been due to somewhat more intense roasting of the steam-treated coffees.

T. H. P.

Study of Aloes and Determination of some of its Constituents. P. Valaer and G. E. Mallory. (*Amer. J. Pharm.*, 1934, **106**, 81-96.)—When drugs such as rhubarb, cascara, frangula, senna and aloes, whose action is determined mainly by resinous hydroxyanthraquinone compounds and other anthraquinone derivatives, are extracted with ether in presence of acid, and the ethereal extract is made strongly alkaline with ammonia, a red colour develops. This test may be used as the basis of the determination of aloes in medicinal preparations. Under controlled conditions, the depth of the colour varies almost directly in proportion to the amount of aloes or other emodin-bearing drug present. In this way the proportion of free emodin bodies is obtained. A similar determination, carried out after hydrolysis with concentrated sulphuric acid, gives the total emodin bodies, the colour being then due to both free and combined anthraquinone compounds. The colours are compared with those obtained in the same way from aloes, and, in view of the wide variations shown by aloes of different origins, it is suggested that only those from Curaçao, which have a high aloin-content, be regarded as official.

In a second colorimetric method, for determining emodins in presence of phenolphthalein, the preparation is treated with ammonia and benzyl alcohol, and the colour developed is measured as before. Whichever method is used, the colour is suitably expressed in terms of the Lovibond red and yellow glasses, and tables are given showing the results thus furnished by aloes of the three recognised varieties, namely, Socotrine (E. Africa), Cape, and Curaçao. Shaffer's gravimetric determination of aloin is satisfactory when applied to about 50 grms. of aloes, but becomes unreliable with preparations containing, together with other drugs

and aromatics, only 4 to 8 grains of aloes per fluid oz. Hager's method is not trustworthy, even with pure aloes, and is still less so with preparations containing invert sugar, etc. T. H. P.

Differentiation Reactions of Argyrol, Collargol, Electrargol, and Protargol. C. Vaile. (*J. Pharm. Chim.*, 1934, **126**, 256-261.)—In order to differentiate the various silver colloids or hydrosols present in a solution, it is necessary to arrange that the concentration of the colloidal silver shall be about 0.07 to 1 per cent. To 2 ml. of a 0.5 per cent. solution of chromic acid is added sufficient of the colloidal solution to give, after shaking, the yellow colour of the chromic acid, more of the solution being used when it is necessary to dilute, so that for a 0.07 per cent. solution, 7 ml. are taken, and for a 1 per cent. solution only 1 ml. From 0.5 to 1 ml. of a saturated solution of sodium carbonate is then added. With argyrol and protargol the first precipitate re-dissolves, but with collargol and electrargol the addition of the alkali to the liquid produces a brick-red precipitate which is clear at first. To differentiate argyrol from protargol, about 9 ml. of silver solution are added to 1 ml. of a 10 per cent. solution of sodium hyposulphite, followed by 3 drops of phenolphthalein solution. In the presence of protargol a rose to red colour results, whilst with argyrol the colour is masked by that of the argyrol itself. To differentiate collargol from electrargol, 5 ml. of the silver solution are added to a mixture of 0.5 ml. of the 0.5 per cent. chromic acid solution and 5 ml. of nitric acid (French Codex). After 24 hours, and often before, the yellow colour of the liquid is replaced by a bluish tint in the presence of electrargol, but no change occurs with collargol. Also, if equal parts of a saturated solution of picric acid and the silver solution are mixed, collargol will give a precipitate after 1 hour, whilst electrargol will not. D. G. H.

Biochemical

Daily Administration of Small Quantities of Aluminium in relation to the Development of Cancer. G. Bertrand and P. Serbescu. (*Compt. rend.*, 1934, **198**, 1100-1102.)—Two series of rabbits were treated, the first by administration of tar alone, and the second by tar in combination with 6 weekly doses of 20 mgrms. of aluminium, given as sulphate. In the first series 78.3 per cent. of the animals living over 40 days died of cancer, and in the second series 50 per cent. In no case where aluminium had been given were any lesions of the stomach or digestive tract found, and even one rabbit which received 50-mgrm. doses per kilo. of body weight over a period of 60 days, produced a litter of six after 28 days. From the 60th day onwards it was also treated with tar and died of broncho-pneumonia on the 162nd day. Its digestive tract was normal. It is concluded that the facts do not support the alleged toxicity of aluminium, and that there is no evidence that the ingestion of aluminium is favourable to the development of cancer. D. G. H.

Evaluation of the Quality of Meat by Artificial Digestion with Pepsin. J. A. Smorodinzew. (*Z. Unters. Lebensm.*, 1934, **67**, 429-432.)—For this purpose use is made of a 0.5 to 1 per cent. solution of an active pepsin containing

sufficient hydrochloric acid to make the p_H value of the solution 1.5 to 1.7. The chopped meat (1 grm.) is digested with 10 ml. of the enzyme solution for 3 hours at 37° C. The extent to which digestion has proceeded is then measured by formol titration of the solution with 0.5 *N* sodium hydroxide solution. Muscle fibre or meat containing it in large proportion is found to be more readily digestible (by 25 to 30 per cent.) than connective tissue or meat consisting largely of this.

T. H. P.

Quantitative Determination of Glutathione. L. Binet and G. Weller. (*Compt. rend.*, 1934, **198**, 1185–1187.)—The method for determining glutathione in vegetable or animal tissue depends on its quantitative precipitation by cadmium lactate in a medium of p_H 6 to 7, without oxidation of the sulphhydryl group. One to 2 grms. of the tissue are cut up and weighed in a tared receptacle containing 5 ml. of 10 per cent. trichloroacetic acid. The tissue is ground with sand, triturated with the acid and a further 5 ml. of acid are added. After 3 to 5 minutes the mass is filtered, the extract is placed in a centrifuge tube, and the extraction is repeated 3 times. Three to four drops of bromthymol blue are added to the united extracts, which are neutralised by first adding a 50 per cent. (by vol.) solution of sodium hydroxide, with constant shaking, and when neutralisation is nearly complete finishing with a 2 per cent. (by vol.) solution of sodium hydroxide until a blue tint, which is stable for about 2 minutes, is formed on adding 1 drop of the alkali. Two ml. of a 1 per cent. solution of cadmium lactate are then added, followed by 1 or 2 drops of the 2 per cent. sodium hydroxide solution, which turn the yellow or green solution back to blue. These operations should not have taken more than 1 hour from the death of the animal. The flocculated precipitate is formed in 1 to 2 hours, and the mixture is then centrifuged at a high speed. The supernatant liquid is decanted, the precipitate is dissolved in 10 ml. of 10 per cent. trichloroacetic acid, and the solution is titrated with a 0.004 *N* solution of iodine in the presence of starch. The necessary correction is found by determining the volume of the iodine solution required to give the first indication of colour with starch in 10 ml. of the trichloroacetic acid. In 32 assays the results varied between the extremes of 98 and 104 per cent., and in determining the addition of pure glutathione to extracts of different tissues the results were 99.31 per cent. for liver extract, 98.48 for suprarenal gland, 100.6 for spleen, and 98.5 per cent. for pancreas extracts. Figures obtained for the organs of the dog were lower than those found by the usual methods, and (as mgrms. per 100 grms. of fresh tissue) averaged: Liver, 130; suprarenal gland, 114; spleen, 102; pancreas, 97; and cardiac muscle, 62.

D. G. H.

Simple Adaptation of Kolthoff's Colorimetric Method for Determination of Magnesium in Biological Fluids. A. D. Hirschfelder and E. R. Serles. (*J. Biol. Chem.*, 1934, **104**, 635–645.)—The magnesium ions of the plasma can be determined colorimetrically with titan yellow or Clayton yellow in alkaline solution after the calcium has been precipitated as oxalate; a pink colour is produced. This method avoids the necessity of precipitating the magnesium either as the phosphate ($MgNH_4PO_4$) or as the hydroxyquinoline compound, and is, therefore, much simpler

and much more rapid than the methods previously used. *Reagents required.*—All reagents used must be free from magnesium and calcium, *i.e.* they must give no trace of pink when tested with sodium hydroxide solution plus a drop of the dye (titan yellow or Clayton yellow), and no precipitate or turbidity on addition of ammonium oxalate. (i) Sodium hydroxide solution approximately 0.4 *N* (1.6 per cent.) concentration. (ii) Dye solution: titan yellow or Clayton yellow, 0.01 grm. per 100 ml. of water. (iii) Ammonium oxalate: 3 grms. per 100 ml. (iv) Colloid-dispersing agent. An approximately 0.5 per cent. suspension of ordinary soluble starch or pure dextrin may be used. *Standard Magnesium Solutions.*—For magnesium determinations the colour produced by diluted alkalis plasma or urine is compared with that produced by 0.0002 per cent. of magnesium. *Standard 1.*—A permanent standard solution containing 0.1 per cent. of magnesium is prepared by dissolving 1 grm. of powdered magnesium in 5 ml. of concentrated hydrochloric acid and diluting with water to 1000 ml. It is preserved by adding 2 ml. of chloroform. *Standard 2.*—Two ml. of standard 1 are diluted to 100 ml. To 1 ml. of the diluted standard are added 7 ml. of colloid-dispersing agent, 1 ml. of 0.01 per cent. titan (or Clayton) yellow solution and 1 ml. of 0.4 *N* sodium hydroxide solution. The tube is stoppered and the contents mixed by inversion. This standard must be freshly prepared; 1 ml. of the mixture \equiv 0.002 mgrm. of magnesium.

Analytical Procedure.—About 5 ml. of blood are placed in a 15-ml. centrifuge tube containing a few small crystals of sodium citrate. The tube is closed with a rubber stopper, inverted three times to mix the contents, and centrifuged at 1500 to 1800 R.P.M. for 15 minutes. One ml. of the plasma is pipetted off into another (graduated) centrifuge tube, 0.5 ml. of 3 per cent. ammonium oxalate solution is added, and then 8.5 ml. of water at 45° C. The tube is stoppered, inverted, kept in a water-bath at 45° C. for 20 minutes, and then centrifuged for 15 minutes. The calcium oxalate precipitate is used for the determination of calcium by the Kramer-Tisdall method (*J. Biol. Chem.*, 1921, **47**, 475). For the determination of magnesium 5 ml. of the supernatant fluid (= 0.5 ml. of plasma) are pipetted off into a test-tube, 3.0 ml. of dispersing colloid are added, and then 1.0 ml. of dye solution and 1 ml. of 0.4 *N* sodium hydroxide solution. The contents are mixed and compared in a colorimeter with standard 2. The light used should be filtered through a colour screen of 0.01 per cent. dye solution. The calculation is (reading of standard/reading of unknown) \times 4 = mgrm. of magnesium per 100 ml. of plasma. If the magnesium-content is too high the mixture must be diluted. A micro-method is described for the accurate determination of magnesium and calcium in 0.1 ml. of plasma. The colorimetric method can be used for the determination of magnesium in urine, if the phosphates are first separated by precipitation with uranyl acetate.

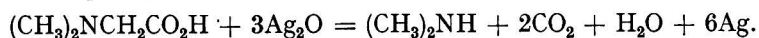
P. H. P.

Reaction of Nitrous Acid with Cystine and Related Sulphur-containing Compounds. S. A. Lough and H. B. Lewis. (*J. Biol. Chem.*, 1934, **104**, 601–610.)—In an effort to explain the anomalous behaviour of cystine in the Van Slyke gasometric method for amino nitrogen noticed by Van Slyke (*J. Biol. Chem.*, 1911, **9**, 185), and further investigated by Schmidt (*J. Biol. Chem.*, 1929, **82**, 587),

a study was made of the reaction of a series of sulphur-containing compounds with nitrous acid. Attempts were made to approach the problem of the reaction between cystine and nitrous acid by securing data along three related lines: (i) When cystine is acted upon by nitrous acid, what degree of oxidation of the sulphur can be obtained? (ii) By the examination of a series of organic compounds in which the type of sulphur linkage varies, is it possible to establish any relationship between the oxidation of the sulphur to sulphate by nitrous acid and production of extra nitrogen in the Van Slyke reaction? (iii) What is the chemical nature of the gas produced when nitrous acid reacts in the Van Slyke apparatus with a nitrogen-free sulphur-containing compound of known purity, the sulphur of which is readily oxidised to sulphate by nitrous acid? The experiments show that the sulphur of cystine was oxidised rapidly to sulphate by nitrous acid, but it was impossible to effect the oxidation of more than 85 per cent. of the sulphur, even over a period of 144 hours, and with the frequent addition of a fresh supply of the oxidising agent. Evidence was obtained to support the contention of Schmidt that the extra nitrogen produced in the reaction between cystine and nitrous acid is related directly to the oxidation of the sulphur to sulphate with the reduction of nitrous acid to nitrogen. When thioglycollic acid reacted with nitrous acid, the gas not absorbed by the alkaline permanganate in the Van Slyke determination was shown by spectroscopic examination to be nitrogen. Since thioglycollic acid resembles cystine in the Van Slyke reaction, in that extra nitrogen is produced and the sulphur is rapidly oxidised to sulphate, it is believed that the "extra nitrogen" in the reaction between cystine and nitrous acid is in reality nitrogen, formed as a result of the reduction of the acid simultaneously with the oxidation of the sulphur.

P. H. P.

Oxidation of Amino Acids by means of Silver Oxide. R. M. Herbst and H. T. Clarke. (*J. Biol. Chem.*, 1934, 104, 769-788.)—In the course of the preparation of dimethylglycine from its hydrochloride it was observed by Clarke, Gillespie and Weisshaus (*J. Amer. Chem. Soc.*, 1933, 55, 4571) that addition of excess of silver oxide to a cold aqueous solution of the latter caused the evolution of carbon dioxide, accompanied by the odours of dimethylamine and formaldehyde. Repetition of this experiment at the boiling temperature showed that the following reaction takes place, with essentially quantitative yields:



As this reaction, if general, might offer certain analogies to the biochemical oxidation of amino acids, its study was extended to other compounds. The results of a series of qualitative tests are shown in a table. The following conclusions are reached:— α -Amino acids are oxidised in hot aqueous solution by silver oxide, with the formation of ammonia, carbon dioxide and aldehydes; the latter may undergo further oxidation to the corresponding acids to an extent depending upon experimental conditions and the volatility and solubility of the aldehyde. Replacement of both amino hydrogen atoms by methyl groups facilitates rather than inhibits the oxidisability, but in betaine this faculty is entirely lost. The presence of hydrogen at the α -carbon atom is not essential to oxidisability. Acylation of the amino group tends to prevent oxidation, but this effect is by no means universal.

P. H. P.

Reaction of Cholesterol with Sulphuric, Selenic and Telluric Acids.

E. Montignie. (*Bull. Soc. Chim.*, 1933, 53-54, 1394.)—(i) On replacing sulphuric acid by concentrated selenic acid in Liebermann's reaction cholesterol gives a pale green colour in 4 or 5 minutes, darkening to a maximum intense green in 30 minutes, whilst the colour disappears on the addition of water. The same reaction occurs very slowly with metacholesterol and stigmaterol. No colour results with a 50 per cent. solution of telluric acid. (ii) If sulphuric acid is added to a solution of cholesterol in chloroform, a red colour is formed (Salkowsky's reaction); selenic acid produces, in a few minutes, a red ring at the point of separation of the liquids; on shaking, the supernatant liquid becomes pink, and at the end of half an hour, brown, and the bottom layer turns pink. With telluric acid the reaction is negative. (iii) In the cold, concentrated sulphuric acid colours cholesterol crystals red; selenic acid makes them grey to greenish-black, and telluric acid gives no colour. (iv) On shaking 50 per cent. sulphuric acid with cholesterol at 100° C. for 1 hour, a mixture of cholesterylenes results, but with 45 per cent. selenic acid only a slight red colour is produced, and the cholesterol is unchanged. With telluric acid no reaction occurs in 1 hour, but if one molecule of the crystallised acid is intimately mixed with 1 of cholesterol and the mixture is kept at 170° to 180° C. for 30 minutes, the mass becomes brown; by taking up the mass with water and then alcohol most of the cholesterol may be recovered unchanged, but on dissolving the mass in benzene a tellurate separates. On evaporating the solvent, dissolving the residue in ether, and adding 95 per cent. alcohol to the solution, 10 per cent. of a white precipitate of cholesterylene (m.pt. 188° to 193° C.) is formed. D. G. H.

Action of Iodine on Cholesterol. E. Montignie. (*Bull. Soc. Chim.* 1933, 53-54, 1412-1414.)—If increasing quantities of iodine are allowed to react with a molar solution of cholesterol dissolved in various organic solvents, by boiling the mixture for one hour and evaporating it on a water-bath, various mixtures of iodine compounds, very difficult to separate, are formed. If, however, instead of evaporating the mixture on a water-bath, the chloroform or benzene solution is treated by repeated washings with sodium thiosulphate, all the iodine which has not reacted with the cholesterol is removed. If the solvent is then evaporated and the residue is taken up with boiling alcohol, a non-saturated black residue remains. The alcoholic solution deposits crystals, which, after several re-crystallisations, melt at 139° to 142.5° C., and consist of a non-saturated substance which takes up bromine in an ethyl acetate medium, giving a mixture of bromides. Acetic anhydride gives a mixture of acetates, the first crystals melting at 92°-95° C., and the last at 105°-110° C. Liebermann's reaction is positive, and the substance, in fact, behaves as a mixture of isomers of cholesterol, probably cholesterol and metacholesterol (m.pt. 139° C.). Allocholesterol is absent, and on treatment with sodium and amyl alcohol the mixture once more yields cholesterol (m.pt. 145° C.). D. G. H.

Contributions to the Study of Marine Products. III. Chemistry of Ostreasterol. W. Bergmann. (*J. Biol. Chem.*, 1934, 104, 553-557.)—Bergmann (*J. Biol. Chem.*, 1934, 104, 317; *ANALYST*, 1934, 294) described the

isolation and properties of a new sterol, ostreasterol, which occurs in the oyster and other molluscs, contains two double bonds, and to which the formula $C_{27}H_{44}O$ was attributed. When subjected to catalytic hydrogenation, ostreasteryl acetate adds 2 molecules of hydrogen and becomes saturated. The determination of the equivalent weight of ostreasterol acetate by saponification gave values which agreed very well with the formula $C_{29}H_{47}O.CO.CH_3$. Therefore the formula for ostreasterol has to be changed from $C_{27}H_{44}O$ to $C_{29}H_{48}O$. The properties of ostreastanol acetate and of ostreastanol, $C_{29}H_{51}O$, were similar to those recorded for sitostanol and sitostanol acetate. Ostreastanol was, therefore, compared, side by side, with a pure sitostanol. The acetates, phenylurethanes and ketones were also compared. From the properties obtained, shown in a table, it is seen that ostreastanol must be considered as identical with sitostanol. The data obtained for ostreastanol are as follows:—Sterol, m.pt., $141^\circ C.$, $[\alpha]_D = +23.73^\circ$; acetate, m.pt., $137^\circ C.$, $[\alpha]_D = +14.58^\circ$; phenylurethane, m.pt., $175^\circ C.$, and ketone, m.pt., $157^\circ C.$, $[\alpha]_D = +41.95^\circ$. It was previously suggested that a tribromo-ostreasteryl acetate described might consist of a mixture of 1 molecule of a dibromide and 1 molecule of tetrabromide. This seems to be the case, for if bromine is added in a larger excess, and the mixture is left standing for a longer time, a well-crystallised bromide is obtained, which melts at $150.5^\circ C.$, and yields a tetrabromide $C_{31}H_{50}O_2Br_4$; this is further proof that ostreasterol contains two double bonds. Ostreasterol is isomeric with stigmasterol, but, on catalytic reduction the latter yields stigmastanol (m.pt., $134-134.5^\circ C.$); thus a difference in the structure of the two sterols is clearly indicated. Cholesterol is regarded as the typical sterol of the animal kingdom. The fact that ostreastanol is identical with sitostanol must be regarded as very significant, because this is the first time that a sterol obtained from animal sources has been converted into a typical plant sterol. It raises the question whether any strict line can be drawn between zoosterols and phytosterols.

P. H. P.

Glucoreductone for the Standardisation of 2, 6-Dichlorophenolindophenol Solutions used for the Determination of Ascorbic Acid (Vitamin C)

Z. I. Kertesz. (*J. Biol. Chem.*, 1934, **104**, 483-485.)—A simple method is presented for the standardisation of the indophenol indicator solution which was proposed by Tillmans, Hirsch and Hirsch (*Z. Unters. Lebensm.*, 1932, **63**, 1; cf. *ANALYST*, 1932, **57**, 260) for the quantitative titrimetric determination of ascorbic acid. Glucose solution heated under standard conditions develops a reproducible reducing capacity towards 2, 6-dichlorophenolindophenol. Under the proposed conditions the resulting solution has a reducing power which is equal to 0.25 mgrm. of ascorbic acid per ml. of reaction mixture, and which may be used for the standardisation of the indicator solutions when ascorbic acid is not available. The experimental procedure used to obtain the solution of the glucoreductone and proposed as standard is as follows:—Five ml. of a 0.5 per cent. solution of Bureau of Standards glucose are placed in a test-tube, followed by 0.5 ml. of 0.5 *N* sodium hydroxide solution, and the tube is closed by a Bunsen valve. The test-tube is immersed in a water-bath at $80^\circ C.$ for exactly 12 minutes, then cooled, and 1 ml. of 10 per cent. hydrochloric acid is added, making a total volume of 6.5 ml. This reaction

mixture is used immediately for titrating a small amount (0.1 to 0.5 ml.) of the indicator solution from a micro-burette according to the modification by Birch, Harris and Ray (*Biochem. J.*, 1933, **27**, 590) of Tillmans' method. After the pink colour disappears the solution is divided into two equal parts, and to one part one more drop of the reaction mixture is added to ensure that the titration has been completed; even with fresh indicator solutions the colour often becomes brownish, but does not change further when more reductone solution is added, and so must be regarded as the end-point. It is shown that the reducing power of the reaction mixture is almost constant between 12 and 15 minutes of heating. Longer heating always lowered the reductone-content of the mixtures, probably owing to further decomposition of the reductone by the alkali. To obtain the value for the ascorbic acid equivalent of the reductone solution a number of 5-ml. samples, taken from different 0.5 per cent. glucose solutions, were used. Calculated for 1 ml. of the indicator solution, they required an average of 2.12 ml. of the heated reaction mixture. The indicator was titrated with a freshly-made 0.1 per cent. ascorbic acid solution. It was found that 2.12 ml. of the reaction mixture and 1 ml. of the indicator were equal to 0.54 mgrm. of ascorbic acid; therefore, 1 ml. of the heated reaction mixture \equiv 0.25 mgrm. of ascorbic acid. P. H. P.

Vitamin-Content of Cod-Liver Oil as influenced by the Nutritional State of the Cod. E. Poulsson and F. Ender. (*Amer. J. Pharm.*, 1934, **106**, 102-106; *Skand. Archiv für Physiol.*)—In Newfoundland the cod fisheries work from July to September, when the spawning is finished, and the cod are well fed and plump, with large livers containing 50 per cent. or more of oil. On the west coast of Norway, however, the fishery operates during the spawning season from January to April, and, as large numbers of fish are taken over a relatively small area and food becomes scarce, the fat stored in the body and in the liver is drawn upon for nourishment. As the fish become leaner, the liver shrinks, and its proportion of fat diminishes. The authors have examined 43 samples of Newfoundland oils and 95 of Norwegian oils for vitamins *A* and *D*. The vitamin *A* was determined by the Carr-Price colour reaction, and vitamin *D* by experiments on rats. The results show that liver-oil from spawning, ill-nourished cod contains a somewhat smaller amount of vitamin *A*, but considerably more vitamin *D* than the liver-oil from well-nourished, non-spawning fish. As vitamin *A* is necessary for the maintenance of the body, even with adult fish, the stores are consumed when the supply of food becomes scarce. On the other hand, vitamin *D* is not consumed by the mature fish, the skeleton of which is completely developed, so that the proportion of this vitamin in the diminished quantity of oil increases. T. H. P.

Histochemical Detection of Iron and Zinc in Citrus Leaves. H. S. Reed and J. Dufrenoy. (*Compt. rend.*, 1934, **198**, 1535.)—Leaves of citrus plants affected with mottle, and green leaves from plants that had been rendered immune by treatment of the roots, 20 months previously, with zinc sulphate, were fixed in a mixture of 95 parts of alcohol and 100 parts of formaldehyde, and embedded in paraffin wax. Microtome sections, 6 μ thick, were cut, and submitted to micro-incineration so as to leave an ash retaining its histological structure. The ferrocyanide reaction showed the presence of iron in the area around the starch

grains, even in leaves deficient in chlorophyll and affected with "mottle." If the ash of a section is treated with sodium nitroprusside (Bradley), crystals of zinc nitroprusside are revealed in abundance in each vacuole enclosing a crystal of calcium oxalate in the leaves from plants grown in soil that had been treated with zinc sulphate. The zinc appears to play a part in the oxidation-reduction equilibrium of the plant. Photomicrographs are given. R. F. I.

Organic Analysis

Volumetric Determination of Formaldehyde in the Presence of Sulphites. J. Eury. (*J. Pharm. Chim.*, 1934, 126, 261-264.)—Since the double sulphite of mercury and sodium in alkaline solution is reducible by formaldehyde, the formaldehyde originally present may be volumetrically determined. Fifty ml. of a 10 per cent. solution of sodium sulphite (to which 1 per cent. of sodium citrate has been added to retard oxidation), 15 ml. of sodium hydroxide solution, and 50 ml. of a mercuric chloride solution containing 278 grms. per litre are placed in a 250-ml. flask, and sufficient of the sample is added to introduce about 0.08 to 0.1 grm. of formaldehyde. The solution is allowed to stand for 15 minutes, with occasional shaking, and is made up to 250 ml.; after standing for 15 to 20 minutes, the mercury is deposited. The liquid is filtered, and the mercury in 100 ml. is determined by the author's modification of the Denigès method (*Bull. Soc. Pharmacol.*, 1930, 37, 599). From this is deduced the quantity of mercury consumed, and thus the proportion of formaldehyde present, 200 parts of mercury being taken as equivalent to 30 of formaldehyde. D. G. H.

New Method for the Determination of Acetyl Values of Lipids, Applicable to Hydroxylated Fatty Acids. E. S. West, C. L. Hoagland and G. H. Curtis. (*J. Biol. Chem.*, 1934, 104, 627-634.)—A new modification of Verley and Bolsing's method of acetylation (*Ber.*, 1901, 34, 3354, 3359; *cf.* Peterson and West, *ANALYST*, 1927, 52, Abst., 607; and Marks and Morrell, *ANALYST*, 1931, 56, 428) is described, in which the hydroxylated substance is treated, hot or cold, with a measured quantity of a mixture of acetic anhydride and pyridine (one volume of anhydride and 7 volumes of pyridine), the excess of anhydride is decomposed with hot water, and the acidity is titrated with standard alcoholic soda after addition of sufficient butyl alcohol to form a homogeneous solution. Acetylation is carried out in stoppered flasks, the stoppers being moistened with pyridine. A new definition of the acetyl value more suitable for calculation is proposed, *viz.* the acetyl value equals the number of mgrms. of acetyl taken up per grm. of substance. The value is found by means of the formula—acetyl value = $(E \times 4.3)/A$, where E represents the ml. of $N/10$ alkali equivalent to anhydride bound, and A the weight of substance acetylated. P. H. P.

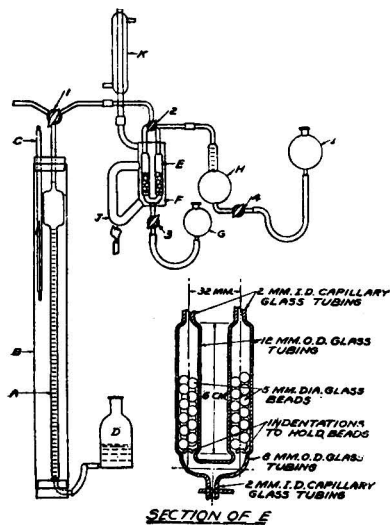
Use of Methoxyacetic Anhydride for the Determination of Hydroxyl Groups. D. W. Hill. (*J. Amer. Chem. Soc.*, 1934, 56, 993.)—An advantage is claimed for methoxyacetic anhydride over acetic anhydride in the determination

of hydroxyl groups, since for the methoxyacetyl derivative formed the methoxyl value may be determined, a procedure which is considered more satisfactory on a micro-scale than the determination of the acetyl value after acetylation. A number of methoxyacetyl compounds have been prepared with the aid of methoxyacetic anhydride by methods similar to acetylation with acetic anhydride.

S. G. C.

Determination of Furfural with Bromine. E. E. Hughes and S. F. Acree. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 123-124.)—At a temperature of 0° C., furfural in dilute hydrochloric acid solution has been found to react quantitatively with 1 molecular proportion of bromine within about 3 to 10 minutes, without any further reactions such as occur as at the ordinary temperature. The furfural solution in 3 per cent. hydrochloric acid is placed in a stoppered flask carrying two side arms, to hold measured volumes of 0.1 *N* potassium bromate solution and 10 per cent. potassium iodide solution, respectively. The flask and contents are cooled to 0° to 2° C. in an ice- and water-bath. The reaction is started by tilting the flask to allow the measured excess of bromate solution to run into the furfural. After 5 minutes, 10 ml. of potassium iodide solution in the other side arm are run into the mixture. The flask is removed from the ice-bath, shaken vigorously to allow the enclosed bromine vapour in the flask to react with the potassium iodide, and the solution is titrated with 0.1 *N* thiosulphate solution, with starch as indicator; 1 ml. of 0.1 *N* potassium bromate solution \equiv 0.0048 gm. of furfural.

S. G. C.



Determination of Butadiene in Gases. H. Tropsch and W. J. Mattox. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 104-106.)—A method is proposed for the determination of butadiene in gas mixtures in which molten maleic anhydride is employed as absorbent. From 2 to 2.5 grms. of freshly-distilled maleic anhydride are heated to approximately 100° C. and drawn into the heated absorber E (Fig. 1) through stopcock 3. The rubber connection to G is replaced, and mercury is introduced into E until all gas is displaced and the molten anhydride stands in the capillaries just above the top of jacket F. By means of mercury from I, all gas is displaced from H and the capillary connection to E. A 100-ml. portion

of the gas to be analysed is taken into the burette, the mercury level in E is lowered to the bottom of the U-tube, and the gas is passed from A, through E, into bulb H, the rate of passage being regulated by adjusting stopcock 4. The gas is then passed back into A, through E, by lowering the levelling bottle D and raising I. The gas remaining in E is displaced by raising the molten maleic anhydride into the capillaries just below stopcock 2. The volume is then read, and the operation

is repeated, once or twice, until no further absorption is observed, the temperature of *E* being kept at 100° C. A preliminary run with a portion of the gas to be analysed should be made in order to saturate the maleic anhydride physically with any hydrocarbons which may be present in the mixture. Olefines are without interference; acetylene may be present without effect in concentration up to 15 per cent.

S. G. C.

Wax-content and Feel of Indian Cottons. N. Ahmad and D. L. Sen. (*J. Text. Inst.*, 1934, 25, 150r.)—The wax-content of 12 Indian cottons varied from 0.229 to 0.544 per cent. on the dry cotton. The feel varied from rough in those of low wax-content to silky in those of higher wax-content. For the determination of the wax, 2.5 grms. of the clean cotton of known moisture-content are extracted in a Soxhlet apparatus with benzene for 4 hours. The extract is filtered hot into a tared weighing bottle and evaporated at 90° C., and the residue is heated to constant weight at 100° C. Ether is too volatile to use in Indian laboratories.

R. F. I.

Colour Reactions of Metadinitrobenzene in Alkaline Medium. Determination of Benzene Vapour in the Air. M. Péronnet and R. Truhaut. (*Bull. Soc. Chim.*, 1933, 53-54, 1464-1474.)—A study of the colour reactions of *m*-dinitrobenzene in alkaline medium has shown that certain aldehydes which give no colour reaction in the cold, give one on heating; that uric acid alone among the purine bases examined gives a colour reaction, and this may be used to identify the acid; further, that creatinine may be distinguished from creatine, since the former gives a positive reaction and the latter none. Certain amino acids give a violet ring with the reagent if 2 ml. of a 10 per cent. alcoholic solution of *m*-dinitrobenzene are superimposed, without mixing, on a solution of 0.1 gm. of the acid in 2 ml. of a 10 per cent. sodium hydroxide solution. Phenyl- β -alanine gives an intense violet colour, but phenyl- α -alanine gives no colour under these conditions.

The determination of benzene vapour in air is based on the transformation of the benzene into the metadinitro derivative by the action of a mixture of concentrated sulphuric acid and fuming nitric acid at a low temperature, and by the colour reaction given by the *m*-dinitrobenzene in alcoholic and alkaline solution with the reducing sugar laevulose. A double bubbler is connected at one end with an aspirating flask, and at the other with a flask which is fitted with a funnel, and into which is introduced, in a small ampoule, a given weight of benzene (10 to 60 mgrms.). The stopcocks are closed, the ampoule is broken, and slight heat is applied to vaporise the benzene. The vapour in the flask is subsequently displaced, with the aid of aspiration, by mercury introduced through the funnel. The first bubbler contains 2 ml. of the sulphuric-nitric acid mixture, and the second, which serves as a guide to total absorption in the first, contains 1 ml. of the same mixture. The benzene is usually all retained in the first bubbler. At the end of the reaction the bubblers are immersed in a sodium chloride freezing mixture and left for 1 hour, after which 5 ml. of water are added, drop by drop. This, incidentally, washes the glass connections, and 14.2 + 4 ml. (under the above conditions) of 25 per cent. sodium hydroxide solution are then added, 12.2 ml. for the first bubbler, and 6 ml. for the second. After being emptied, the bubblers are washed out several

times with 25 ml. of 95 per cent. alcohol. The clear liquid is decanted, the precipitate is washed with 70 per cent. alcohol, and the liquid and washings are made up to 100 ml. The alkalinity should be 0.125 *N*, and between 25 and 125 mgrms. of *m*-dinitrobenzene should be present. To 10 ml. of the liquid are added 10 ml. of a 1:200 solution of laevulose in 70 per cent. alcohol, the mixture is rapidly filtered, and the filtrate is held at 25° C. for 20 minutes. A comparative test is made at the same time with a known quantity of benzene and with 3 ml. of the sulpho-nitric mixture. It is found that the intensity of the violet colour superimposed on the yellow (which cannot be quite eliminated, even when working at a low temperature) is proportional, when compared in a colorimeter, to the quantity of benzene present.

D. G. H.

Detection of Small Amounts of Pyridine, particularly in Burnt Wood.

A. Brüning and M. Schnetka. (*Chem.-Ztg.*, 1934, **58**, 156-157).—For solutions over 1:1000 in strength, precipitating agents (*e.g.* tannin, picric acid, Nessler's reagent or potassium ferrocyanide) may be used. Cadmium chloride is unsuitable on account of the time required to produce its characteristic precipitate, but potassium iodide, bromine water and mercuric chloride act more rapidly. For dilutions of 1:10,000 use may be made of the crystalline precipitate produced with gold chloride or of the violet colour produced by 1-chloro-2,4-dinitrobenzene in the presence of alkali. For dilutions of 1:100,000 the cyanogen bromide reaction of Goris and Larsonneau (*Bull. Sci. Pharmacol.*, 1921, **28**, 497) has been suggested, the reagent being prepared (after C. Göpner, *Z. angew. Chem.*, 1901, 355) by adding 1.6 ml. of sulphuric acid (sp.gr. 1.84) to a solution containing 2 grms. of sodium bromide and 1.5 gm. each of sodium bromate and sodium cyanide in 70 ml. of water. This reagent, which decreases in sensitiveness after 1 week, is added to the pyridine solution together with 1 drop of aniline, when a red precipitate is produced in dilutions of 1:100,000, and a red colour in dilutions of 1:1,000,000. The colour is due to the bromide of α -anilido-*N*-phenyl-dihydro-pyridine (*cf.* W. König, *ibid.*, 1905, p. 115, and *J. prakt. Chem.*, 1904, pp. 69, 105, who showed that various colours were obtainable by varying the nature of the nitrogen compound used). Tests on the steam-distillates from the extracts in water of the residues from woods which had been soaked with pure alcohol or distilled spirit and ignited, indicated that furfuraldehyde also gives the Goris-Larsonneau reaction, the presence of this substance in such distillates being confirmed by the reaction with aniline and acetic acid. In both reactions the intensity of the red colour depends on the p_H value, and is increased by the presence of an excess of aniline in the former case, but decreased in the latter. Other substances which occur in wood-tar (*e.g.* alcohols, aldehydes, ketones, organic acids, phenol, guaiacol, pine wood oil) gave no colour which might be confused with that given by furfuraldehyde and pyridine in the cyanogen bromide reaction, and numerous other organic substances present did not interfere; the tobacco alkaloids (nicotine, nor-nicotine and 2- β -pyridyl piperidine), α - and β -picoline, the steam distillates from pyrolygneous acid, *pix liquida* and *oleum rusci* gave strongly-positive reactions. A selective reaction for pyridine, in the presence of furfuraldehyde is as follows:—In 5 ml. of a neutral or weakly-acid solution of the sample are dissolved 1 to 2 grms. of solid sodium

acetate (to serve as a buffer), and then 0.5 ml. of the above cyanogen bromide reagent and 1 ml. of a saturated aqueous solution of benzidine are added. After 1 minute at room-temperature, a carmine-red colour develops in the presence of α - or β -picoline or of 1 part in 10,000 to 1,000,000 of nicotine or pyridine; wood tar, tobacco smoke and roasted coffee also gave a positive reaction, but no pyridine was indicated in the steam-distillate obtained after extracting wood from burnt conifers. The amount of air present during combustion is probably an important factor in determining the presence of pyridine, since when various nitrogenous substances (*e.g.* leather, flesh, etc.) and various woods were heated in a retort, pyridine was detectable in the distillate, whilst the steam distillate obtained from the residue when ignition occurred in the open air gave a negative reaction.

J. G.

Inorganic Analysis

Colorimetric Determination of Lead. S. Feinberg. (*Z. anal. Chem.*, 1934, **96**, 415–418.)—The lead is converted into molybdate, and the molybdenum is determined colorimetrically with thiocyanate after reduction with stannous chloride. The lead (0.1 to 1.7 mgrm.) is conveniently obtained by anodic deposition. The anode is treated, drop by drop, with hot hydrochloric acid, the solution is diluted to 40 ml., neutralised with ammonia, acidified with 15 to 20 drops of acetic acid, and treated, while boiling, with 10 to 15 ml. of 0.5 per cent. ammonium molybdate solution. When coagulated after some minutes' boiling, the precipitate is collected on a small pad of filter pulp, and washed with water containing a little acetic acid. The pad is then washed 7 or 8 times with 5-ml. portions of 10 per cent. sulphuric acid, the cold solution being treated first with 10 ml. of 5 per cent. potassium thiocyanate solution and stirred, then with 5 ml. of 10 per cent. stannous chloride solution in hydrochloric acid (1 : 4), and, finally, diluted to 100 ml. with 10 per cent. sulphuric acid. The orange-yellow colour is matched against that of a standard molybdenum solution (0.2 to 0.25 gm. MoO_3 in 10 ml. of 1 : 1 sulphuric acid, and diluted to 500 ml.). The molybdenum-content of the quantity of standard solution taken should closely approximate that of the unknown solution, but should not be higher; the standard solution is run into 50 to 60 ml. of 10 per cent. sulphuric acid contained in a colorimeter cylinder, thiocyanate and stannous chloride being added in order. If the colour of the standard solution is slightly weaker than that of the unknown a few drops of the molybdenum solution may be added to the former.

W. R. S.

Glycerin as a Reagent for Mercury. M. Stschigol. (*Z. anal. Chem.*, 1934, **96**, 328–333.)—Glycerin reduces alkaline mercury solutions, the metal being precipitated. The solid substance or the solution is shaken with 10 per cent. potassium iodide solution, treated with 30 per cent. caustic soda solution, and filtered. The filtered solution is treated with a little more alkali, and boiled for some minutes after addition of 1 ml. of glycerin. The presence of mercury is indicated by a black precipitate or the darkening of the liquid. For quantitative purposes, 0.2 to 0.4 gm. of the material is dissolved in water or a suitable acid, and the solution is boiled with 20 to 30 ml. of 30 per cent. alkali and 5 to 10 ml. of glycerin for 5 minutes.

The addition of glass beads is recommended. The liquid is diluted to about 100 ml. and filtered through a double paper. The precipitate is washed with water until free from chloride and alkali, and dissolved in 10 to 15 ml. of hot nitric acid (sp.gr. 1.4). The solution is diluted with 50 ml. of water and treated with permanganate until faintly pink, and the tinge is just removed with ferrous sulphate. The cold solution is titrated with 0.1 *N* ammonium thiocyanate solution in presence of ferric alum; 1 ml. is equivalent to 0.01003 grm. of mercury. W. R. S.

Determination of Mercury in Galenicals, and its Separation from Bismuth. E. Schulek and S. Floderer. (*Z. anal. Chem.*, 1934, 96, 388-398.)—The material is dissolved in, or extracted with, 5 per cent. hydrochloric acid; addition of a little bromine water is necessary for calomel. Mercury is extracted from ointments by solution in chloroform and agitation with dilute hydrochloric acid; gelatin preparations are hydrolysed by boiling with hydrochloric acid (reflux condenser). Organic mercury compounds and preparations containing vegetable substances are destroyed by strong sulphuric acid and hydrogen peroxide in a distillation flask connected with a receiver, to avoid loss of mercury if chlorine is present. The mercury solution is precipitated with hydrogen sulphide, and the precipitate is dissolved in sulphuric acid and hydrogen peroxide; the mercury is then titrated by Volhard's thiocyanate method. Bismuth does not interfere in the titration, which may be carried out in sulphate or nitrate solution; halogen, cyanide, and cyanate interfere. If a determination of bismuth is also required, a separation is achieved by means of hydrogen sulphide in a solution containing 20 per cent. of hydrochloric acid; less than 4 per cent. of bismuth should be present. The mercury precipitate is washed free from bismuth with the 20 per cent. acid, preferably by centrifuging and decanting. The washed precipitate, which contains combined chlorine, is dissolved in a little bromine water, the excess of bromine is removed with hydrazine, and the mercury is once more precipitated as sulphide, this time in an easily filterable form free from chlorine. W. R. S.

Gravimetric Determination of Copper, Cadmium, and Nickel as Complex Mercury Compounds. A. Taurins. (*Z. anal. Chem.*, 1934, 97, 27-36.)—Methods are described for the precipitation of $[\text{Cu}(\text{NH}_3)_4] [\text{HgI}_3]_2$ with 4.912 per cent. Cu, of $[\text{Cd}(\text{NH}_3)_4] [\text{HgI}_3]_2$ with 8.375 per cent. Cd, and of $[\text{Ni}(\text{NH}_3)_6] [\text{HgI}_3]_2$ with 4.434 per cent. Ni, from ammoniacal solutions by means of mercuric potassium iodide. The precipitates are collected on a porous crucible, washed with alcohol and then with ether, and weighed after being dried *in vacuo*. Nickel may thus be separated from cobalt, after oxidation of the latter in ammoniacal solution by means of hydrogen peroxide. Full details are given in the original. W. R. S.

Volumetric Determination of Tin with Potassium Iodate. J. B. Ramsay and J. G. Blann. (*J. Amer. Chem. Soc.*, 1934, 56, 815-818.)—Stannous tin in dilute hydrochloric acid solution under an atmosphere of carbon dioxide may be determined by titration with standard potassium iodate solution, a slight excess of iodate being added, as shown by the liberation of iodine, which is back-titrated with standard thiosulphate solution, with starch as indicator. The most suitable concentration of acid is 1 *N*, a slight negative error being produced in

more strongly acid liquid. In connection with the reduction of stannic tin to the stannous state by the aid of zinc, it was found that the tin sponge would re-dissolve more rapidly if a little cobalt or nickel chloride had been added to the solution, an effect which is considered to be due to co-precipitation of cathodic particles of cobalt or nickel.
S. G. C.

Benzoate Method for the Precipitation of Iron, Aluminium and Chromium. I. M. Kolthoff, V. A. Stenger and B. Moscovitz. (*J. Amer. Chem. Soc.*, 1934, **56**, 812–815.)—The precipitation of the hydroxides of the iron group in the presence of ammonium benzoate is claimed to yield a precipitate more readily filterable and less liable to occlude other ions than usual. The procedure is to add ammonia to the slightly acid solution until the precipitate formed redissolves very slowly; 1 ml. of glacial acetic acid and sufficient ammonium chloride to yield about 1 per cent. concentration are added, and about 20 ml. of ammonium benzoate solution (10 per cent.) for every 65 mgrms. of aluminium, or 125 mgrms. of iron or chromium present, are added, with stirring. The suspension produced is boiled gently for 5 minutes, or for 20 minutes if chromium predominates. The precipitate is filtered off on a coarse filter-paper, and washed ten times with hot water containing 1 per cent. of ammonium benzoate and 2 per cent. of glacial acetic acid, to prevent peptisation. For exact work, the filtrate and washings should be evaporated to about 50 ml. for the recovery of incompletely precipitated iron or chromium. The results of test experiments showed that the co-precipitation of zinc, manganese, cobalt, nickel and calcium was slight but definite, particularly in the presence of much trivalent metal. Under the conditions employed, partial precipitation of, *e.g.* lead and copper, occurs in the absence of hydroxides of the iron group.
S. G. C.

Determination of Manganese with Anthranilic Acid. H. Funk and M. Demmel. (*Z. anal. Chem.*, 1934, **96**, 385–388.)—Manganous anthranilate (16.80 per cent. Mn) is white and crystalline, and a little more soluble than the metallic compounds previously described (*ANALYST*, 1933, **58**, 241, 567). Hence the precipitation is carried out in small bulk and with a large excess of sodium anthranilate. The neutral solution (0.1 gm. Mn, 80 ml.) is treated with 60 ml. of 3 per cent. reagent. The precipitate is collected, after one hour's standing, in a porous crucible, and washed with 0.5 per cent. reagent and then with alcohol, and dried at 105° to 110° C. The bromimetric titration of the precipitate may be carried out as already shown (*ANALYST*, 1933, **58**, 361).
W. R. S.

Colour Reactions of Rhenium. B. Tougarinoff. (*Bull. Soc. Chim. Belg.*, 1934, **43**, 111–114.)—Ferrocyanide and dimethylglyoxime give characteristic colours in presence of stannous chloride. The ferrocyanide test is carried out as follows:—One ml. of neutral or acid perrhenate solution is treated with a few drops of 5 per cent. potassium ferrocyanide solution and 2 to 3 ml. of stannous chloride reagent (25 grms. of salt in 100 ml. of strong hydrochloric acid). The resulting colour is pale brown to red-brown. The addition of water produces a purple colour, which permits of the identification of 0.01 mgrm. of rhenium. Sulphate does not interfere, but nitrate in concentration above 0.5 *N* does. The following

elements mask the reaction: nickel, cobalt, chromium, tungsten, vanadium, and niobium; hence, rhenium must be separated from them by distillation with strong sulphuric acid at 190° C. (thermometer in liquid) in a brisk current of air. The distillate is received in a solution containing ferrocyanide and stannous chloride, a rose-red colour after 15 to 20 minutes' distillation indicating rhenium. Molybdate solutions give a golden-yellow precipitate if free from rhenium; a small admixture of that metal causes the precipitate to turn brownish-yellow. For the dimethylglyoxime test, 1 ml. of perrhenate solution is treated with a few drops of the alcoholic solution of the reagent, and stannous chloride as before. The resulting colour is yellow to deep red, according to the quantity present. The yellow colour turns green on warming; the deep-red solution assumes a green fluorescence under those conditions. It is possible thus to identify 0.01 mgrm. of rhenium in the presence of several other metals; if a precipitate forms, it is separated from the warmed liquid by filtration; a green filtrate indicates the presence of rhenium.

W. R. S.

Analytical Reactions of Rubidium and Caesium. W. J. O'Leary and J. Papish. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 107-111.)—The analytical literature on rubidium and caesium is critically reviewed. Caesium and rubidium may be quantitatively precipitated and separated almost completely from potassium by the addition of luteophosphomolybdic acid (9-phosphomolybdic acid, Kehrmann and Böhm, *Z. anorg. Chem.*, 1894, 7, 406), which is prepared by heating the commercial dodeca-phosphomolybdic acid at 300° to 350°C. until it changes in colour from orange to green, and then extracting and crystallising the solution of the green material. The caesium and rubidium precipitates were of somewhat indefinite composition; they were therefore converted into chloroplatinates after removal of the molybdenum as sulphide. Recovery of upwards of 99 per cent. of the rare alkali metals (calculated as chlorides) was thus obtained from mixtures with up to 100 parts of potassium nitrate. Modifications of the silicotungstate and chloroplatinate methods are described.

S. G. C.

Applications of Chloramine in Volumetric Analysis. A. S. Komarowsky, W. F. Filonowa, and I. M. Korenman. (*Z. anal. Chem.*, 1934, 96, 321-328.)—Chloramine (sodium *p*-toluenesulphochloramine, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NNaCl}$) is a cheap substitute for iodine (*cf.* ANALYST, 1927, 52, 668). The authors have applied it to the determination of ferrocyanide, thiocyanate, hydrazine, hypophosphite, and carbon disulphide. The solution used (15 grms. per litre, which is nearly 0.1 N) was standardised against arsenious oxide in presence of starch and very little potassium iodide, as well as against an acidified solution of potassium iodide, the liberated iodine being titrated with thiosulphate.

Ferrocyanide.—The titration must be carried out in weakly acid, not in neutral or alkaline solution. The ferrocyanide (about 0.4 gm.) is dissolved in 100 ml. of water, in a glass-stoppered flask, and the solution is treated at 40° C. with 5 ml. of 0.5 N hydrochloric acid and 20 ml. of chloramine solution. The excess of the latter is then ascertained by addition of 0.8 gm. of sodium bicarbonate and a known excess of arsenite solution, which is titrated with chloramine after addition of starch and a crystal of potassium iodide.

Thiocyanate.—The solution (100 to 150 ml.) is treated with 2 grms. of bicarbonate and 50 ml. of chloramine solution, and left in the dark for 4 hours at ordinary temperature. The excess of reagent is then determined by addition of 20 ml. of 2 *N* hydrochloric acid and 1 to 2 grms. of potassium iodide, with subsequent thiosulphate titration; or by arsenite in excess, which is titrated by chloramine in presence of starch and a crystal of iodide.

Hydrazine.—A 0.1 *N* solution (10 ml.) is treated with 0.5 gm. of bicarbonate in 15 ml. of water, a crystal of iodide, and starch solution, and titrated slowly with chloramine, with constant stirring.

Hypophosphite.—The results are serviceable, but slightly lower than by iodimetric titration. A solution of calcium hypophosphite (1 gm. in 250 ml. of water) is treated with 10 ml. of sulphuric acid (1 : 5) and 30 ml. of chloramine solution. After 24 hours, 2 grms. of potassium iodide are added, and the iodine is titrated with thiosulphate.

Carbon Disulphide.—This is dissolved in 5 per cent. alcoholic potash. The solution is made just acid with acetic acid, treated with sodium bicarbonate, and titrated with chloramine after the usual addition of a little iodide and starch. Kept in the dark, the chloramine solution was found to maintain its titre for 40 days.

W. R. S.

Determination of Fluorides in Natural Waters. J. M. Sanchis. (*Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 134–135.)—In connection with the question of the mottling of tooth enamel caused by the presence of fluoride in drinking water, the following modification of the zirconium–alizarin method has been adopted for the determination of the fluoride: To 100 ml. of the water, filtered, if necessary, and to the prepared standards noted below, are added 2 ml. of 3 *N* hydrochloric acid, 2 ml. of 3 *N* sulphuric acid and 2 ml. of indicator solution (prepared by mixing equal volumes of a 0.17 per cent. solution of sodium alizarin sulphonate and a 0.87 per cent. solution of zirconium nitrate crystals as a stock solution, and diluting 20 ml. of this to 100 ml. as required). The solutions are brought rapidly to the boiling-point and then cooled. Four hours after cooling, or on the following day, the colour of the sample solution is compared with those of the standards in Nessler tubes. The use of a range of nine standards is suggested, *viz.* 0, 2.5, 5.0, 7.5, 10, 15, 20, 25, and 30 ml. of standard sodium fluoride solution (1 ml. \equiv 0.01 mgrm. of fluorine) made up to 100 ml. with distilled water. A slight reddish precipitate, due to appreciable quantities of organic matter or phosphate, which may appear in the solution after cooling, should be dispersed prior to the colorimetric comparison, but in extreme cases, where the amount of precipitate is sufficient to prevent satisfactory comparison, the method of Willard and Winter (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 7), or its modification by Boruff and Abbott (*id.*, 1933, 5, 236), should be employed. The following have been found not to interfere: chloride, sulphate, bicarbonate, sodium, calcium, and magnesium up to 500 parts per million; manganese up to 200 parts per million; silicate up to 50 parts per million; phosphate, boron, copper, and iron up to 5 parts per million; sulphide up to 2 parts per million. Samples of natural waters from 11 sources in the Los Angeles district gave results from 0.3 to 2.1 parts per million of fluorine.

S. G. C.

Microchemical

Collected References. Detection and Determination of Small Amounts of Cholesterol and other Sterols. A. Wasitzky. (*Mikrochem.*, 1934, 14, 289-310.)—Most of the methods are described briefly, and some more important methods in detail. Ten references are given on methods of detection of cholesterol. The quantitative methods are divided into:—(i) Colorimetric (46 references); (ii) spectrometric (6 references); (iii) nephelometric (1 reference); (iv) gravimetric (10 references); (v) volumetric (16 references); (vi) other methods (6 references).

J. W. B.

Micro-Determination of Iodine and a Useful Micro-Desiccator. W. Münster. (*Mikrochem.*, 1933, 14, 23-26.)—The Pregl method of iodine determination is modified by utilizing Vieböck and Brecher's titration method (*Ber.*, 1930, 63, 3207) for the determination of methoxyl, to replace the weighing of silver iodide as the final stage of the determination. The Pregl combustion tube, containing a glass spiral, is replaced by an ordinary micro-combustion tube, 50 cm. in length, and 0.7-0.8 cm. in diameter. One end is attached to a narrow tube, about 0.2 cm. diameter, and 18 cm. long, bent down at right angles to the combustion tube. A small bulb of the same diameter as the combustion tube may be blown in the tube just before the right angle bend, but, although this is useful in preventing any sucking-back of the absorption liquid, it is not indispensable. This narrow outlet tube dips into the absorption liquid in a drawn-out test-tube, in the way used in the methoxyl determination. The combustion is carried out in the usual way in a stream of washed oxygen at the rate of 8 bubbles in 10 seconds; this passes over the substance which has been weighed into a platinum boat and introduced into the combustion tube. The vapours pass over the heated platinum contacts, and are finally absorbed in 2 to 3 ml. of a solution of bromine in acetic acid, as used by Vieböck and Brecher (*loc. cit.*). The combustion is complete in 10 minutes, after which the apparatus is allowed to cool in a stream of oxygen. Finally, the absorption apparatus is washed, and the liquid is transferred to a conical flask containing a few ml. of sodium acetate solution, and, after destruction of the bromine, the iodate is titrated against *N*/100 thiosulphate solution. A complete analysis may be carried out in less than 1 hour. Very good results are obtained from substances with high iodine-content.

A useful micro-desiccator for vacua higher than the Pregl type is made in three parts, attached by ground-glass joints:—(i) A bulb (about 50 ml. capacity) containing phosphorus pentoxide; (ii) a tubular portion which fits in the Pregl drying block contains the boat and substance; (iii) a glass tap which connects with the suction-pump through a tube containing calcium chloride. J. W. B.

Micro-Determination of Silica in Tissues and in Blood. G. Rodillon. (*Bull. Biol. Pharm.*, 1934, 1, 33-59.)—This is a modification of Isaacs' method (*Bull. Soc. Chem. Biol.*, 1924, 6, 157), already modified in different ways by King (*Biochem. J.*, 1933, 27, 990), and as used by Parri and Scotti (*J. Pharm. Chim.*, 1933, 125, 513). The method consists in (i) Decomposition of organic matter,

by fusing about 0.05 gm. of the dried and powdered tissue with about 8 times its weight of sodium bicarbonate, with, if necessary, the addition of a few small crystals of ammonium nitrate. (ii) Formation of the silico-molybdate, by adding 1 ml. of 10 per cent. ammonium molybdate solution to the solution of the ash in 2 drops of dilute nitric acid and a few drops of 30 per cent. sulphuric acid and heating to 60° C. To prevent the interference of phosphates, 1 ml. of 95 per cent. alcohol is added to the molybdate solution, and, after the addition of the solution of the ash, 1 ml. of a solution of ammonium citrate (2 grms. of citric acid, 10 grms. of water, and 10 ml. of concentrated ammonia) is added. (iii) Reduction of the silico-molybdate, by means of two reducing agents—hyposulphite and hydroxylamine—to give a blue colour. The sodium hyposulphite (0.35 gm.) and hydroxylamine hydrochloride (0.35 gm.) are added to the test-solution and dissolved without heating, and the mixture is diluted to 10 ml. (iv) The blue colour of the solution is compared in a colorimeter, after filtration, if necessary, with that given by a standard solution of silica. J. W. B.

Rhodizonic Acid as an Indicator in the Volumetric Determination of Barium. A. Friedrich and S. Rapoport. (*Mikrochem.*, 1933, 14, 41-48.)—Rhodizonic acid is unsuitable as an indicator for the determination of barium in acid solutions, as the end-point is dependent on the rate of titration. Unreliable results were also obtained in neutral solution, owing to the fact that the rhodizonate is present as an almost insoluble suspension colloid, and also is inactivated by the precipitated barium sulphate. By the addition of gelatin solutions better results are obtained by titration in neutral solutions, but a comparison with the end-point colour must always be made. Small amounts of barium may be precipitated with sodium rhodizonate in the presence of gelatin, and the barium in the suspension may be determined colorimetrically by means of a Pulfrich photometer. The coloured solution is sensitive to light. J. W. B.

Physical Methods, Apparatus, etc.

Identification of Tanning Agents under the Quartz Mercury-Vapour Lamp. L. Pollak. (*Coll.*, 1933, 628; *J. Text. Inst.*, 1934, 25, A200.)—A fabric is used consisting of wool through which silk and mercerised cotton threads are drawn in the warp direction and rayon and cotton threads in the weft. Pieces of this fabric (5 × 5 cm.) are immersed for 30 minutes in a boiling water-bath in 50 ml. of a solution containing 2 or 4 grms. of the liquid tannin extract per 100 c.c. and 2 ml. of 2 per cent. acetic acid, and then washed and dried. Daylight and filtered ultra-violet light show different effects on the different threads. The characteristics of a variety of extracts are tabulated. In most cases the cellulosic fibres are scarcely tinted, but show a distinctive fluorescence in ultra-violet light, the colour varying with the nature of the tannin extract. R. F. I.

Fading [Tests for Dyes]. J. Grant. (*Proc. Tech. Section, Paper Makers' Assoc.*, 1934, 14, 335-347.)—Methods of carrying out fading tests, with special reference to dyed and undyed paper, are critically reviewed. Neither the filtered nor unfiltered light from the mercury or carbon arc is completely satisfactory for

reproduction of the effect of exposure to daylight, although the latter is preferable, and both give misleading results in some cases. As a standard method it is suggested that typical dyes from each of the basic, acid and direct dyestuff classes should be exposed for total periods of 1, 2 and 3 weeks, respectively, at 20 to 23° C. and 60 per cent. relative humidity, between 10 a.m. and 3 p.m., to a cloudless north sky during June and July, nine such standards being chosen so as to provide for a red, yellow and blue dye in each class. In order to carry out the test, the sample is exposed at any time or place simultaneously with a duplicate of whichever standard it most closely resembles in properties and shade, until it has faded to the same extent as the faded standard; the change in colour so produced in the sample can then be taken as due to reproducible conditions of exposure. As this is slow, especially in the winter, and cannot be used at night, it is further suggested that the change in appearance in filtered ultra-violet light produced by exposure to unfiltered ultra-violet light from the mercury arc should be taken as an indication of the change in appearance in visible light produced by exposure to visible light. A numerical expression of fastness to light may then be obtained from the minimum period required to produce the first change plainly visible to the naked eye, and this may vary from a few minutes for a fugitive dye to many hours for a fast dye. The method is subject to the same limitations as the direct use of ultra-violet rays as a fading agent, but gave reliable indications for about 75 per cent. of the dyes tested. It is very useful for routine tests and for work with dyes the properties of which are known, but may give misleading results in certain cases, *e.g.* when a particularly fast dye or pigment colour is used, and the paper itself changes in appearance first. In all such tests the lamp should be allowed to run for 5 minutes in order to eliminate the effect of the ozone usually produced during this initial period. Applications of the method to various problems of paper technology are described (*cf.* Bromley, *ANALYST*, 1933, 58, 29). J. G.

Reviews

HANDBUCH DER LEBENSMITTEL-CHEMIE. Vol. II. ALLGEMEINE UNTERSUCHUNGSMETHODEN. Part I. PHYSIKALISCHE METHODEN. Edited by A. BÖMER. Pp. 536. Berlin: Julius Springer. 1933. Price 66RM. (69RM. bound).

As its title indicates, the second volume of this monumental treatise deals with general processes available for the investigation of foodstuffs, and this part with physical methods. The general scheme of the Handbuch has already been noticed in *THE ANALYST* (1933, 58, 503), and the volume now considered continues the same comprehensive thoroughness. Each chapter describes the theory underlying the methods, and their application, giving a description and the mode of use of the various instruments employed. The subjects include specific gravity, viscosity, ultrafiltration, dialysis, surface tension, solubility, melting-point and boiling-point, cryoscopy, calorimetry, p_H , indicators, oxidation-reduction potentials, conductivity, refractometry, spectroscopy, polarimetry, colorimetry, luminescence analysis and microscopy. Chemical and biological methods are promised us in Part II.

The method of treatment seems to be uniformly thorough and, so far as the reviewer can check it, good. There is much to be said for the mode of presentation adopted; suppose one has a melting- or boiling-point to determine on a small quantity of some unusual material, reference to this volume shows at a glance all, or nearly all, the good methods, both macro and micro, so that one can proceed without having to hunt up special journals. Similarly, all the types of instrument for, say, refractive index or viscosity are explained. The method does, however, lead to certain omissions which may perhaps be rectified when we reach volumes dealing with special subjects; thus, there are described several cryoscopes, but not that of Hortvet, which we now all use for our milk samples. Ostwald's, Engler's, and Holde's viscometers are described, but in England Redwood's is the most popular; and tables or formulae connecting the results obtained by these instruments would be useful. The section on quantitative fluorescence analysis is perhaps most novel, and is not usually found in books connected with foods; quinine salicylate, chlorophyll and haematoporphyrin afford examples of its use. Microscopy covers not only matters instrumental, but also section-cutting, staining, photography, histology, and some aspects of bacteriological technique.

The book is concise, encyclopaedic, well written and well produced, and is to be commended, but it costs twice what it should.

H. E. Cox

LABORATORY MANUAL OF COLLOID CHEMISTRY. INTRODUCTORY COLLOID CHEMISTRY. By H. N. HOLMES. Pp. xvii+229 and xiv+198, respectively. London: Chapman & Hall. 1934. Price 20s. and 15s. 6d. respectively.

It is a somewhat difficult matter to review each of these books dispassionately, since, in spite of individualised titles, the one is merely a reprint of the other. However, to start with the *Laboratory Manual*: this is a concise, well-written, and amazingly comprehensive book, well calculated to give any reader an insight into the variety and charm of colloid chemistry and to stimulate the desire to know more of the subject. Short and clear directions are given for carrying out numerous experiments, and a running commentary, explaining briefly the background of these, forms a brief but adequate introduction to the theory of the subject.

Besides the experiments, described in detail, there are numerous well-chosen references to descriptions of original work which can be used as a basis for other work. A commendable feature of the book is that the student is encouraged to use his initiative in planning experiments and in deducing the theoretical inferences to be drawn from work he has carried out.

There is a good bibliography of text-books on colloid chemistry, in which the author particularly recommends his own *Introductory Colloid Chemistry* as a helpful introductory manual. While fully endorsing this description, the reviewer cannot help feeling that any student who has bought the *Laboratory Manual* will receive a disagreeable shock when he finds that for fifteen and sixpence laid out in purchasing the *Introductory Colloid Chemistry* about three and sixpence purchases new matter and about twelve shillings merely purchases matter lifted, paragraph by paragraph, and figure by figure, from the *Laboratory Manual*. It is true that

the chapters on "Emulsions," "Gels and Jellies: Solvated Colloids," and "Viscosity and Plasticity," have been largely re-written, and that the chapter on "Adsorption from Liquids" contains a reasonable amount of fresh matter. These, however, form only a small proportion of a book in eighteen chapters. It seems a pity that this additional matter was not incorporated in the *Laboratory Manual*, and, considering that the latter is now, deservedly, in its third edition, the publishers could well have done this without raising the price. The *Introductory Colloid Chemistry* need then never have been launched as a separate text-book. The reviewer feels, somewhat strongly, that the student of colloid chemistry may be recommended to buy either of these books—but not both.

D. JORDAN LLOYD

THE ANALYSIS OF OIL FOR PRODUCTION OF LUBRICANTS. ARTHUR A. ASHWORTH, M.A., A.M.I.C.E., M.Inst.P.T. Pp. 63 with 7 plates. London: Ernest Benn, Ltd. 1933. Price 9s. net.

This little book is devoted entirely to one highly specialised process of analysis, *viz.* the estimation of the lubricating oil-content of a crude petroleum or raw stock. It describes clearly and in very great detail the succession of operations involved and various apparatus which have been specially devised for the purpose. The oil after neutralisation is distilled in a pipe-still under a pressure of about 5 to 10 mm. (unless asphaltic matter is absent, when this distillation may be omitted), and chemically refined by treatment with about 5 per cent. sulphuric acid, decantation from the acid tar, and agitation with a decolorising clay and filtration. The filtered oil is then fractionated by distillation from a glass flask under 5-mm. pressure, and from an examination of the viscosities of the fractions, the yield of various lubricating oils, from light spindle oil to heavy cylinder oil, may be calculated.

Such a book, as a whole, can be of interest to only a very limited number of readers, but some of the apparatus described is capable of much more general application, as, for example, a pressure filter, suitable for the filtration of very viscous liquids, which consists of a piece of 3-inch steel pipe, one end of which is closed with a screw cap, through which is inserted an ordinary bicycle tyre valve, whilst at the other end is fitted a disc of fine-meshed copper gauze on to which may be clamped a double thickness of filter-paper. There is also a novel fractionating receiver for collecting a large number of fractions during a vacuum distillation, and a slight modification of the B.E.S.A. U-tube viscometer, better suited to the examination of liquids of high viscosity.

The author is to be congratulated both on the skill with which he has devised the necessary apparatus and on the lucidity with which it is described. There is one small error, however, which might be liable to cause confusion. The unit of kinematic viscosity is throughout the book described as the "poise," whereas it should be the "stoke."

W. H. SIMMONS

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. 1933. Vol. 18. Price 7s. 6d. to members, 12s. 6d. to others.

If any fault can be urged against the Annual Reports on the Progress of Applied Chemistry, it is that they are too eminently readable. The busy man hurriedly consulting one section is likely to find himself browsing, willy-nilly, in others. To the industrial chemist the book will be a veritable anthology, to be dipped into again and again.

The names of the contributors afford sufficient guarantee that no work of importance has escaped mention. Possibly, a team of literature searchers devoting their full time to the task might discover faults of omission, but certainly in the fields known to the present reviewer the importance of any work passed over is entirely a matter of personal opinion.

Whilst the various reports will be indispensable to specialists, the introductory paragraphs of each might well be read by all who take an intelligent interest in life, whether they be by profession technicians or not, for nowhere are there so readily available equally unbiased and authoritative reviews of the conditions prevailing in modern industry, and the layman, equally with the scientist, could not fail to profit by their perusal. The world depression of the last few years has emphasised how interrelated are all fields of human endeavour, and none, scientist, politician, economist, banker, and business man alike, can afford to ignore the work being done outside his own particular department. All branches of civilisation stand or fall together, so that it is pleasing to note the spirit of optimism which permeates most of these reviews. Even if in 1933 there have been few dramatic and spectacular discoveries to record, this volume shows that, in applied chemistry, as in all other directions, it was a year of steady progress and recovery.

E. W. PATES

EASILY INTERPOLATED TRIGONOMETRIC TABLES WITH NON-INTERPOLATING LOGS, COLOGS, AND ANTILOGS. F. W. JOHNSON, M.A. America: The Simplified Series Publishing Co. Price: From 1 dollar 60 to 4 dollars, according to cover.

The avowed object of this set of tables is to eliminate the operation of interpolation in the use of mathematical tables. This it contrives to do in the case of five-figure logarithms by giving the log for numbers from 10,000 to 99,999, and, in the case of trigonometrical functions, by including a table of proportional parts alongside the one consulted. The tables are also thumb-indexed, so that any appropriate table can readily be found. These features combined should do much to avoid waste of time when the user has become really accustomed to the method of reading the tables, which is novel and, to one more used to the normal form, rather confusing. The author prefers not to use negative characteristics for logarithms, and does this by adding 10 in such cases. This practice and the need for special rules in certain cases call for some mental effort to attain a degree of accuracy in reading compatible with the accuracy of the tables themselves, which are stated to be "always correct to the last figure given."

P. BILHAM

SPIRIT TABLES FOR USE WITH SIKES'S A & B HYDROMETERS. Issued under the Authority of the Commissioners of H.M. Customs and Excise. H.M. Stationery Office, London. 1933. Pp. 68. Price 2s. 6d. net.

The present Tables, legalised by "The Strength and Weight of Spirits Ascertainment Regulations, 1930" (S.R. & O., 1930, No. 328), have been compiled by the late Sir Edward Thorpe and Sir R. Robertson, assisted by members of the Government Laboratory staff. Part I gives directions for the use of Sikes's A and B Hydrometers, followed by two tables, II and V. Table II is for use with the A hydrometer, or B hydrometer with A poise; it covers a temperature range of 30–100° F., by separate degrees, with an extreme range of alcohol strengths, 57.5–75.4 per cent. over proof; at 60° F. the range is 66.7–73.5 per cent. over proof. Table V, for use with the B hydrometer without the poise, covers a temperature range of 47–100° F., with extreme range of alcohol strengths 65.9–75.3 per cent. over proof, at 60° F. the range is 73.5–75.3 per cent. over proof. The wide temperature range obviously renders the instruments serviceable under diverse climatic conditions. Part II gives directions and two tables (IV and VI), for determining the weight, per gallon of spirits, in pounds to three decimal places. Tables IV and VI are to be used with Sikes's hydrometers, as mentioned above, for Tables II and V, respectively. Though no temperature is stated, it is probably assumed that the indications apply to the standard temperature, 60° F.; should the determination be made at another temperature, this must be stated.

This little volume will undoubtedly prove of great service to those who have to deal with high-strength spirits, and praise is due to all who shared in its compilation. Though it seems unfortunate that we still adhere to an arbitrary "Proof spirit" standard, doubtless there are very good reasons for not making a change to a more logical and up-to-date standard.

F. M. CORY

Publications Received

- THORPE'S DICTIONARY OF APPLIED CHEMISTRY.** Supplement. Vol. I. A to M. Edited by J. F. THORPE and M. A. WHITELEY. Pp. 680. London: Longmans, Green & Co. 1934. Price 60s. net.
- ORGANIC CHEMISTRY BY VICTOR VON RICHTER.** New Translation by E. N. ALLOTT. Pp. 790. London: Kegan Paul & Co. 1934. Price 35s. net.
- ORGANIC SYNTHESSES.** Vol. XIV. W. W. Hartan, Editor-in-Chief. Pp. 100. London: Chapman & Hall. 1934. Price 10s. 6d. net.
- ANNUAL REPORT FOR 1933.** Central Narcotics Intelligence Bureau. Egyptian Government. Pp. 168. Cairo. Price P.T. 10.
- BIBLIOGRAPHY OF CHLOROPICRIN, 1848–1932.** By R. C. ROARK. U.S. Dept. Agriculture. Miscellaneous Publications No. 176. Washington. Price 10 cents.