THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

NORTH OF ENGLAND SECTION

THE Third Summer Meeting was held at the Queen's Hotel, Scarborough, from July 1st to 4th. The attendance numbered sixty-one, including many ladies.

Among those present were the following:—Past Presidents (Mr. A. Chaston Chapman accompanied by Mrs. Chaston Chapman, Mr. E. R. Bolton, Dr. Dunn with Mrs. Dunn); Hon. Secretary (Dr. G. Roche Lynch); Hon. Treasurer (Mr. E. B. Hughes with Mrs. Hughes); Editor of THE ANALYST (Dr. C. A. Mitchell); Mr. E. M. Hawkins; and Miss Elliott.

On Saturday afternoon Mr. E. R. Bolton read a paper on "The Edible Fat Industry, with Special Reference to Hydrogenation." A telegram was sent to the President (Mr. F. W. F. Arnaud) expressing the regret of the members that he was unavoidably absent. A resolution of congratulation was passed unanimously to Dr. W. R. Schoeller on his receipt of a Beilby Memorial Award mainly for work done under the Analytical Investigation Scheme.

The Chairman (Mr. John Evans) extended a cordial welcome to all attending the meeting, especially those from the south. He also proposed a resolution, which was passed unanimously, conveying the greetings of the Section, and expressing its goodwill and loyalty to the Council.

Various forms of recreation were enjoyed, and Dr. Dunn rendered pieces of music from old English masters. On Sunday afternoon the party proceeded by motor through Whitby to Sandsend Hotel, where tea was taken. Perfect weather conditions prevailed throughout the meeting.

A clever cartoon, entitled "A Few Ancient Analysts," was specially drawn by Mr. G. L. Wollaston for the menu of the dinner on July 2nd.*

A vote of thanks to the Hon. Secretary of the Section (Mr. J. R. Stubbs) was proposed by the Chairman, and passed unanimously.

* Copies of this cartoon can be obtained, free of charge, on application to the Honarary Secretary of the North of England Section (Mr. J. R. Stubbs).

Obituary

CECIL HOWARD CRIBB

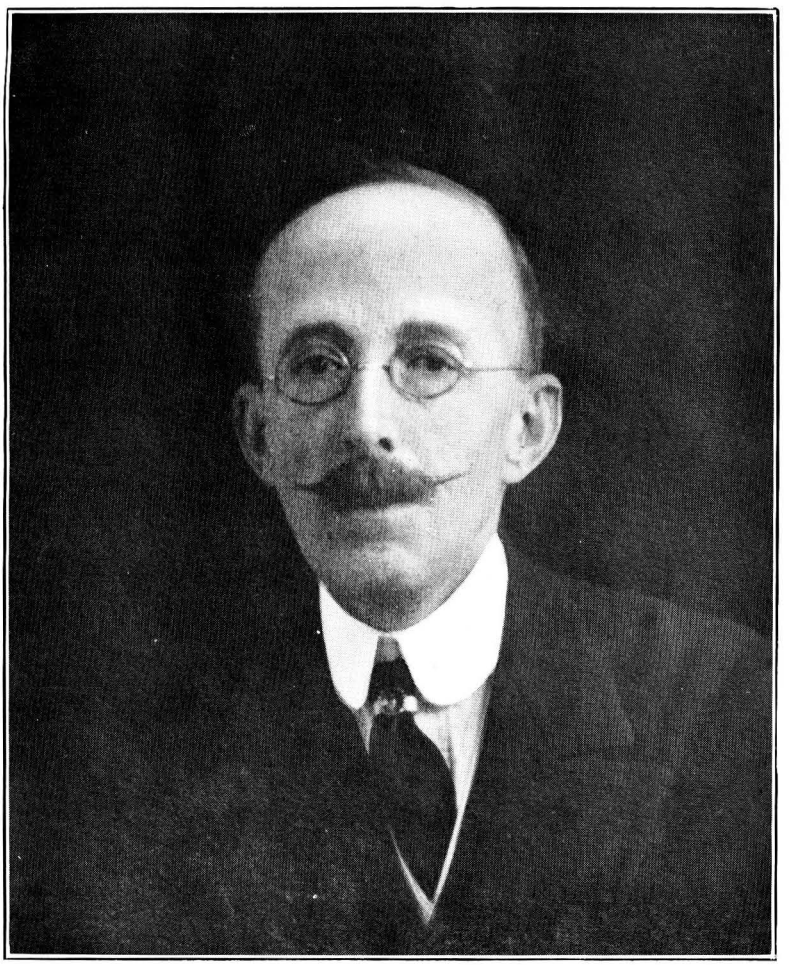
THE announcement of the death of Cecil H. Cribb in the July issue of THE ANALYST must have been read by his many friends with great regret. On June 11th Cribb was taken seriously ill and, despite an operation, he passed away on the 13th. He was 68 years of age. By his death the Society loses one of its most ardent supporters, for, after his election as a Member in January, 1890, Cribb took a very deep interest in the affairs of the Society. From 1895 onwards he served, on different occasions, as a Member of Council, and also for two periods as a Vice-President. Since 1908 he served on the Publication Committee of THE ANALYST, the interests of our journal being dear to him, and up to the last month he read the proofs with unfailing assiduity and attended the prolonged meetings of the Committee with unflagging zeal. He was also greatly interested in the work of the Institute of Chemistry, and was the first Examiner (1907–1911) in the Chemistry of Foods and Drugs under the scheme of examinations introduced during the Presidency of Professor P. F. Frankland.

He received his early education at a boarding school at Leatherhead and at University College School, and about 1878 proceeded to the School of Mines, South Kensington, where he studied under T. H. Huxley and Sir Edward Frankland, among others. For nearly two years he acted as assistant to Professor Purdie, at St. Andrews University, where his manipulative skill and ingenuity proved valuable in devising lecture experiments. Afterwards he became assistant to Professor P. F. Frankland. In 1887 he registered as a medical student at University College Hospital, and covered a large part of a medical course, though he never qualified.

In the early eighties he opened a laboratory in London, and commenced practice as an analytical chemist, and this practice he carried on until his death. His first public appointment was that of Public Analyst to the Strand Board of Works (1886), and in those early days, if the food samples submitted were few in number, they provided a very considerable amount of work, owing to widespread adulteration. When the Strand became incorporated in the City of Westminster, Cribb became a joint Public Analyst for that City. The other important public appointment which he held was that of Public Analyst for the Metropolitan Borough of Fulham. During the nineties he took part, in collaboration with H. H. F. Hyndman, in experiments on the then recently discovered *X*-rays. His private practice was considerable in extent, and included the examination of a number of waters, for he was consulting analyst to several Water Companies.

The late hour to which he stayed in his laboratory every evening is a proof of his zeal for work, and those who had the privilege of working with him can testify to his ability and to his versatile brain. He revelled in attacking a difficult problem, and many days, or even weeks, would pass before his ingenious mind would exhaust phases of work which might yield the desired result.

Cribb will long be remembered for his resourcefulness in introducing new forms of chemical apparatus. Probably he is best known as the inventor of the double-surface condenser. It might well be said that until Cribb attacked the



Neil H. Britt

methods used for the condensation of vapours in the laboratory, the Liebig condenser or a worm condenser were accepted as irreplaceable pieces of apparatus. Condensers a foot or a yard in length were reverenced, and few people had even thought that any other form of condenser was possible or permissible in a laboratory. Cribb really showed that a 4-inch upright condenser could work as efficiently as many feet of glass tubing surrounded with water. Commercially he met with a similar difficulty, that of convincing anyone that there was any apparatus that could work as efficiently as the old type of condenser. His carbon dioxide apparatus is familiar to many. This apparatus and his specific gravity bottle have features which should have made them even more popular than they have become. However, his ingenuity was by no means restricted to devising apparatus for use in the laboratory, for many other conceptions were the subject of patents taken out by him. During the cycle craze, about 1897, he invented a bicycle head which by easy treatment could be made to lock the steering of a cycle This device was actually purchased by a cycle company. Then an automatic machine for the delivery of postage stamps received his attention, but the device was in advance of public opinion, or possibly requirements.

In 1900, Cribb published a paper on "The Influence of Temperature and Pressure on the Saline Constituents of Boiler Water." This paper showed the decomposition of various salts which occurs when waters are concentrated under pressure, etc.

Papers then followed describing the new forms of carbonic acid apparatus, and also the double-surface condenser mentioned above.

In 1905, the results of an investigation, carried out in conjunction with another investigator, were published, showing the action of slightly alkaline waters on iron. Papers written in conjunction with others were published later: on "A Method for the Approximate Determination of Boric Acid," "Analyses of Cream Cheese," "The Facing of Rice," "The Analysis of Margarine," and, a very important contribution at that date, "The Composition and Analysis of Chocolate."

He was joint author with H. Mansfield Robinson of the book "Law and Chemistry of Foods and Drugs."

Cribb was an enthusiastic collector of antiques, and of old prints chiefly relative to chemistry, and he acquired a very considerable knowledge of these. His collection of prints of the alchemists and their laboratories was very large and representative, and he also possessed many pieces of old scientific apparatus.

His recreations included cycling, lawn tennis and gardening. Though never of robust constitution, he spared himself no physical effort; in fact, he had a great belief in exercise, and for many years he cycled between his old home at East Finchley and his laboratory in the West End of London. Only the recent crowded state of the thoroughfares, and his health, made him forsake his cycle for the train. He was devoted to dogs, having a predilection for the largest breeds.

A man of broad outlook, a deep thinker, a scientist with a gift of easy conversation—how all who knew him must miss him! The sadness of his old friends at his graveside was a token of the deep affection of his fellow men for him, and the presence of so many was an appreciation of the services he so unstintingly rendered to the profession.

F. W. F. ARNAUD

Castor Seed in Feeding Stuffs

By F. ROBERTSON DODD, F.I.C.

(Extract from a paper read at the Meeting of the North of England Section, February 13, 1932)

Opinions are divided as to the desirability of stating definitely the quantity of castor which may be present in a feeding stuff, or of fixing any limit which must not be exceeded. Dr. Voelcker, Chemist to the Royal Agricultural Society, regards the giving of percentage figures for castor seed present as being utterly misleading, owing to the uneven distribution of the castor. He accordingly declines altogether to certify to percentages present, but condemns a food as unfit for use if he finds castor in it. Force of circumstances, however, compels most of us who handle the raw materials as they enter the country to state the percentages, since the new contracts specify limits.

For the County Analyst, who receives a much smaller sample than we at the ports of entry, any trace of castor seed should be sufficient to condemn the parcel, and there should be no need for him to state quantities.

When the controversy arose some years ago, my late partner suggested to the trade that a limit of 0·005 per cent. of castor seed should be fixed, but Liverpool merchants regarded this limit as too risky, and agreed to insert in the contract a clause to the effect that, if any one of three analysts found any trace of castor seed, the buyer could reject the parcel.

An unwritten opinion is current that any quantity of castor seed over 0·01 per cent. may prove fatal to cattle. This, so far as I know, is without foundation, beyond the fact that castor poisoning has occurred when no analyst has found more than 0·02 per cent. Owing to rumours which circulate in the business world, the question is now being asked whether there is a difference in the toxicity of various species of castor seed. This rumour is persistent, and does not lack the support of certain chemists. "Some castor seeds may be harmless," says the rumour, "whilst others may be deadly." To my mind there is only one course open to the County Analyst, namely, to regard all castor seeds as deadly, and to report accordingly.

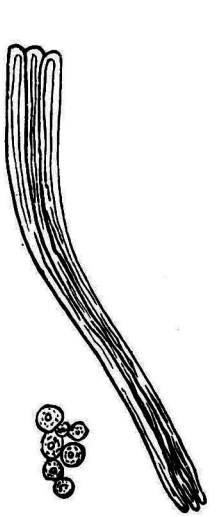
While the general details of the method for the detection of castor seeds are, doubtless, familiar to most, there may yet be some points, gathered by me in a lengthy experience, which may be found useful.

My own laboratory generally receives a sample of 7 to 10 lbs. in weight. This is broken into small pieces and quartered down, the quartered portion being passed through a mill, which reduces it to pass a sieve with ten meshes to the inch. This ground portion is passed through a Clarkson sampling machine, and the portion delivered is weighed and used for one test. The process is repeated on the portion of the original sample first broken down, until four samples of 50 to 120 grms. have been obtained.

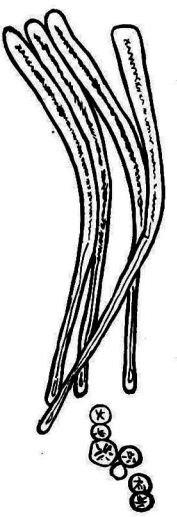
In doubtful cases further portions are prepared and treated. Certain analysts weigh 1 lb. of the sample and use that for their test, but I prefer to prepare a number of samples in the way described, the total quantity being generally between 250 and 500 grms.

The portions selected are treated with 500 c.c. of dilute sulphuric acid (1·25 per cent.), and, then after being washed by decantation, with 300 c.c. dilute sodium hydroxide solution (1·25 per cent.). The washing after the treatment with sodium hydroxide may be very important. In such materials as kapok seed cake, for example, the colouring matter is very difficult to remove and interferes with subsequent bleaching.

A solution of calcium hypochloride, sufficient to bring the liquor, in which the fibres are suspended, to a strength of approximately 1 per cent. of "available" chloride, is added and the mixture stirred frequently during the bleaching process.



Castor



Croton

For linseed cakes, the fibres of which are easily bleached, half the above strength of hypochlorite suffices. Last year certain "Russian" linseed cake contained a rather high percentage of castor seed, which bleached readily under ordinary conditions. Whether this was immature seed or not I cannot say; I merely record my experience.

As a rule, the bleaching process should not occupy more than an hour. At the end of that time the sample is washed by decantation and spread out on a white dish, and the black particles are picked out and examined under the microscope. Finally, the residue is washed quickly with dilute hydrochloric acid to remove the last traces of hypochlorite, and then with water, and again picked over, to recover any pieces of husk which have escaped the former search.

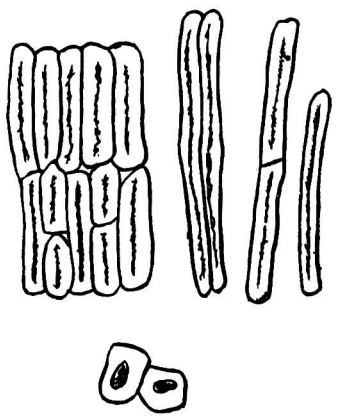
Certain foreign makers have lately been grinding seed much more finely than formerly for the extraction of the oil, and the castor-seed husk is so comminuted that it may occur in very minute particles, which are difficult to see and separate.

Identification under the microscope is, at present, the subject of adverse criticism by shippers, who accuse English chemists of incompetence, and several of us have had letters stating that we have mistaken mustard or hemp seeds for castor.

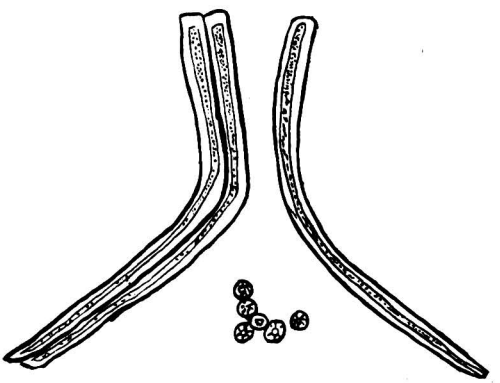
The seeds which might easily be mistaken for castor include grape or raisin seed and ucuhuba seed (possibly), both of which are harmless; croton seed and curcas seed, both more poisonous than castor.

It is usual to return castor, croton or curcas as castor seed. Ucuhuba seed presents little difficulty, but grape seed often presents a real difficulty.

Often one finds on the inner side of grape-seed husk a membrane, not unlike a finger print, which is never found on castor-seed husk, but more often there is little except the size of the "pin holes" to distinguish the two. I am referring to the blackened grape seed from wine-making processes, not to the light seeds, which bleach well.



Grape



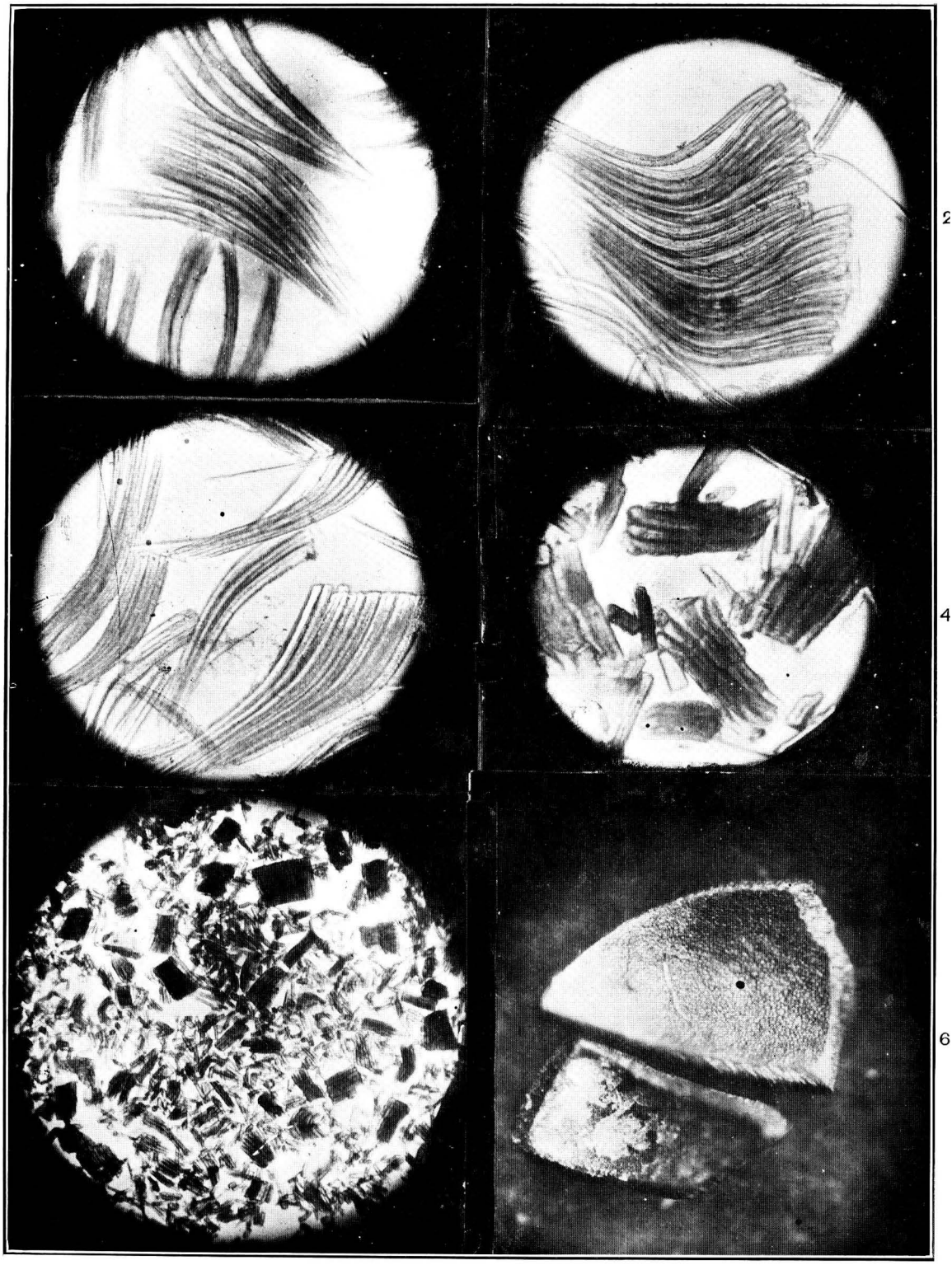
Curcas
Palisade cells and upper surface view

The black grape husks picked out, when treated with sulphurous acid, turn purple fairly quickly, whilst the castor husks remain black for a long time.

If the husks be treated with 50 c.c. of $N/2$ hydrochloric acid and 4 grms. of potassium chlorate on a water-oven for about an hour, the palisade cells separate, and can be examined under a $\frac{1}{6}$ in. objective, when there need remain no doubt in the mind of the observer.

The diagrams, drawn with the aid of a camera lucida by a former assistant, Mr. O. A. Morch, slightly exaggerate the points to be looked for. The photographs taken by my assistants, Messrs. Telford and Waters, explain themselves. The magnifications are approximately 40 and 140. As a closing note, I may add that, when stating percentages, the system adopted in Germany is now generally required, *i.e.* the London contracts have copied the German rule of stating the percentage of castor-seed *husk* found.

The chemical treatment to which a meal is subjected before picking out the husks, extracts from castor-seed husk substances amounting to one-fifth of its weight, *i.e.* 80 per cent. only is found.



(1) Castor × 140 (2) Curcas Palisade cells × 140 (3) Croton × 140 (4) Grape × 140
(5) Grape × 40. Mixed fibres (6) Castor and Grape × 40. Husks with top-light illumination

The custom, based on the average fibre content of castor seeds, is to weigh the husk found and multiply this weight by 5 to express the percentage of seed.

The weight of the husk increased by one-fourth should represent the castor-seed *husk* originally present.

An alternative method is to multiply the weight of the husk by 5 (= castor seed), and to divide this result by 4 (= castor-seed husk originally present).

(See also J. W. Leather, ANALYST, 1892, **17**, 121; Lander and Geake, *id.*, 1914, **39**, 292; Brioux and Guerbet, *id.*, 1921, **46**, 100; H. Waites, *id.*, 1922, **47**, 306; Report of Case, *id.*, 1932, 381.)

DISCUSSION

The PRESIDENT welcomed Mr. E. E. Billington, not only as a member of the Society, but also as a manufacturer who could present the manufacturers' view to the meeting.

Mr. BILLINGTON joined issue with Mr. Dodd on the statement that analysts should condemn feeding stuffs if they contained a minute trace of castor seed. He had experimented in the feeding of cattle with cakes containing 0·001 per cent. of castor seed without ill effects. He gave details of several cases of castor-seed poisoning which had been investigated, and contended that the analyst was not merely a detective and judge combined, but one to whom the community looked to investigate such subjects and to suggest measures to counteract the effects of the poison. The introduction of small quantities of castor seed into feeding stuffs was never intentional and, so far as chemical control on arrival at Liverpool and in reputable works was concerned, every attempt was made to prevent its inclusion. Other feeding stuffs could be substituted for pea nut (arachis) meal, but these would affect the fat of the milk, and particularly the character of the butter made therefrom, and manufacturers, wishful to do their best for their customers, were compelled, by monetary considerations, to use the best available materials. In spite of the most rigorous control, traces of castor seed occasionally found their way into the products, and, in cases where the total quantity present was very minute, he thought that the analyst should be merciful in his report. With regard to the acceptance by continental importers of parcels which this country had rejected, there was another reason than that given by Mr. Dodd. By the time the chemist's report was issued, showing that castor seed was present, the consignment was in barges many miles away, and the expense of bringing it back and re-delivering it to the sellers would be so great that buyers accepted delivery, *but* demanded an allowance.

Professor W. H. ROBERTS drew attention to the fact that cattle could be immunised to castor seed.

Mr. J. HANLEY confirmed this, and mentioned the different reactions of various animals to the poison. Some of his experiments (made under licence) had shown that, whilst one animal died from consuming a mixture containing castor seed, others not only showed no ill effects, but throve on the mixture. The difficulty was that when a number of animals were fed on beans and one of the animals promptly died, one could not decide whether it was a case of poisoning or of idiosyncrasy of the animal. He instanced also a case of human idiosyncrasy of an assistant who, within half-an-hour of chewing beans of unknown origin (which he did not swallow) developed a red rash all over his body. The rash did not disappear for a few days.

Mr. S. E. MELLING asked whether, in view of its well-known de-toxicating properties, active carbon had ever been tried on animals suffering from the poison; if not, he suggested that such treatment was worthy of consideration.

Mr. A. R. TANKARD mentioned that, during the war, investigations made in Hull on behalf of the Ministry of Agriculture and Fisheries, had shown that it was possible to treat castor seed in such a way as to render the meal quite innocuous to live stock. He asked whether it was possible to apply any simple method to distinguish such treated meal from the actively poisonous material.

A general discussion followed, in which questions as to the action of the lipase or enzyme; the occurrence of castor seed in various materials; the effect on workers with castor seeds, etc., were mooted.

Messrs. Dodd and Billington received the thanks of the meeting for their valuable contributions to the discussion.

An Improved Method of Titrating Arsenic Precipitated by Hypophosphorous Acid*

BY B. S. EVANS, M.C., PH.D., F.I.C.

THIS paper is to be taken as supplementary to one published in 1929 (Evans: "A Method for the Separation and Determination of Arsenic," ANALYST, **1929, 54**, 523), in which directions are given for the precipitation of arsenic by hypophosphorous acid, and its subsequent determination by solution in a measured excess of standard iodine solution and titration of the excess of iodine with arsenious acid. It was shown in that paper that with the filters then in use the "blank" could be eliminated by titrating away the iodine with a small excess of the arsenious solution and then titrating the excess of arsenic again with standard iodine (*ibid.*, p. 523). When the method was carried out in this way no appreciable "blank" was found. This method was in use, with excellent results, until recently, when an unforeseen difficulty made itself manifest. It will be noted that the principle of the method of titration was the entire removal, by an excess of arsenious acid, of the iodine absorbed on the filter pulp and giving rise to the blank; it was now found that, owing, presumably, to a change in the manufacture of the filter paper, the intense blue colour of the latter in presence of iodine could not be removed with any reasonable excess of arsenious solution. As this "blueing" of the pulp made it practically impossible to get an end-point by the original method, I attempted to substitute benzene for the starch in the preliminary titration, only adding starch for the final titration. The following results were obtained:

Arsenious acid, *N*/100 solution Taken	Titration	Arsenious acid, *N*/100 solution Found	After deduction of blank
c.c.	c.c.	c.c.	c.c.
1·0	17·3—12·2= 5·1	2·0	1·2
2·0	18·1—10·3= 7·8	3·1	2·3
3·0	23·0—12·5=10·5	4·2	3·4
4·0	20·7— 8·0=12·7	5·1	4·3
5·0	21·5— 5·9=15·6	6·2	5·4
Blank	12·2—10·2= 2·0	0·8	

* Communication from the Research Department, Woolwich Arsenal

It is at once apparent that, although an end-point was now obtainable, the undesirable "blank" had reappeared. A trial of different filtering media did not lead to any improvement; asbestos gave a "blank" similar to that of paper pulp; glass wool did not retain the arsenic precipitate; different powders (*e.g.* sand, kieselguhr, etc.) either let the arsenic precipitate through, or else filtered with extreme slowness. I next tried to eliminate filtration altogether, and, with it, the blank due to the filter pulp, by shaking the precipitated arsenic out with benzene, separating the aqueous layer, and adding the standard iodine solution to the benzene suspension, when the arsenic dissolved with surprising promptness. The excess of iodine could now be titrated directly with arsenious oxide solution after the addition of sodium bicarbonate. This method, though interesting and having possibilities, gave uncertain and generally low results, probably owing to air-oxidation of the precipitated arsenic; with the higher amounts a trace, which had escaped extraction by the benzene, was often found in the aqueous layer. The following results were obtained:

	Arsenious acid, *N*/100 solution Taken c.c.	Titration c.c.	Arsenious acid, *N*/100 solution Found c.c.
(*a*)	1·00	9·7 − 7·1 = 2·6	1·04
(*b*)	1·00	14·3 − 11·9 = 2·4	0·96
(*c*)	2·00	14·5 − 9·3 = 5·2	2·08
(*d*)	4·00	14·5 − 5·4 = 9·1	3·64
(*e*)	5·00	19·6 − 8·0 = 11·6	4·64

In the case of (*d*), filtration of the aqueous layer yielded a minute amount of precipitated arsenic, which, on treatment, brought the amount of arsenic recovered up to 3·80 c.c. This method was abandoned.

As, however, the pulp used for filters quite obviously reacted with iodine, being stained an intense dark blue, wherein it differed from that used in the original investigation, it seemed probable that some reactive substance had been introduced in the manufacture and could be removed by suitable treatment. I found, on trial, that a thorough treatment with bromine removed all difficulty; on the other hand, the use of benzene as an indicator in the initial titration proved to be a definite improvement, and so was retained. The details of the process finally adopted are as follows:

PREPARATION OF PULP.—The pulp is prepared by shaking the torn-up filter paper with a mixture of 1 part of a saturated solution of bromine in hydrochloric acid, with 7 parts of water. When the paper is sufficiently disintegrated the flask is heated on the steam-bath for half-an-hour, and the liquid is then diluted with about its own volume of water, again shaken, and preserved in this state for use. When required for filtering an arsenic precipitate the filter is made in the ordinary way, thoroughly washed with water until perfectly white (*e.g.* 5 washings), and the liquid requiring filtration is then poured on to it.

TITRATION.—After the precipitate has been filtered off and washed, as already described (ANALYST, 1929, **54**, 523), the remaining wash-liquor is shaken out of

the stem of the funnel, the funnel is inverted over a wide-mouthed beaker, and the filter is transferred to the beaker by inserting the jet of a wash-bottle into the stem of the funnel and blowing sharply; the sides and stem of the funnel having been rinsed into the beaker, an excess of standard iodine is immediately added, and the pulp is thoroughly broken up with a glass rod. After standing for a minute or two, about 5 c.c. of benzene are added, and the beaker is gently shaken; about 1 grm. of sodium bicarbonate is then added, and the liquid is immediately titrated with standard arsenious oxide solution until the aqueous liquid has turned completely white and the red colour of the benzene has started to fade; about 1 grm. of potassium iodide is now added, and the titration is continued, with vigorous shaking, until the benzene is quite decolorised, 2 to 3 drops being added in excess. The titration is finished in the way originally described, by adding a further 3 to 4 grms. of sodium bicarbonate, about 30 c.c. of water and a little starch solution, and titrating with standard iodine solution; it must be noted that the end-point, which is quite sharp, is brown and not blue. The calculation of results is as before, *i.e.* 1 c.c. of $N/100$ iodine used in dissolving the arsenic $\equiv$ 0·00015 grm. of arsenic. Results obtained by this method were as follows:

	Arsenious acid, $N/100$ solution Taken c.c.	Titration c.c.	Arsenious acid, $N/100$ solution Found c.c.
(*a*)	5·00	22·3 − 9·9 = 12·4	4·96
(*b*)	4·00	20·0 − 10·1 = 9·9	3·96
(*c*)	3·00	15·2 − 7·3 = 7·9	3·16
(*d*)	3·00	16·4 − 9·0 = 7·4	2·96
(*e*)	2·00	14·8 − 9·8 = 5·0	2·00
(*f*)	1·00	11·6 − 8·7 = 2·9	1·16
(*g*)	1·00	10·8 − 8·0 = 2·8	1·12

The slightly high results in (*c*), (*f*) and (*g*) are probably due to the presence of a rather large amount of hydrogen sulphide or sulphur dioxide in the air at the time the precipitates were being dissolved in iodine solution. A point that came to light during this investigation is that it is dangerous to let the precipitated arsenic stand longer than necessary, since it has a tendency to re-dissolve, owing, presumably, to air-oxidation.

The Determination of Minute Amounts of Copper in the Presence of Iron and Certain other Metals

By L. A. HADDOCK, B.Sc., A.I.C., and NORMAN EVERS, B.Sc., F.I.C.

(*Read at the Meeting, May* 4, 1932)

In 1908 Marcel Delépine published in the *Comptes rendus* (**146**, 981) a paper dealing with the properties of the metallic dithiocarbamates, including the copper salt, and in the same year he published a paper (*Bull. Soc. Chim.*, [IV], **3**, 652) on the detection of traces of copper and iron by means of a solution of a dialkyl dithiocarbamate.

Callan and Henderson (Analyst, 1929, **54**, 650) applied the test quantitatively, and suggested the use of sodium diethyldithiocarbamate as a reagent for the determination of traces of copper. They stated that iron gives a brown colour with the reagent, which interferes with the copper colour, but that iron can be completely removed without loss of copper by precipitating it with ammonia as ferric hydroxide.

Grendel (*Pharm. Weekbl.*, 1930, **67**, 913, 1050, 1345) suggested the electrolytic deposition of the copper, solution of the deposit in acid, and repetition of the process to remove the last traces of iron. The copper is then determined in the solution by means of sodium diethyldithiocarbamate, the colour being shaken out with carbon tetrachloride and compared with the standard in a micro-colorimeter. Elvehjem and Lindow (*J. Biol. Chem.*, 1929, **81**, 435), in applying the copper pyridine thiocyanate method to the determination of minute amounts of copper, found it necessary to precipitate the copper as sulphide in order to avoid interference by iron. The method was also found unsuitable in the presence of calcium phosphate. Chalk (Analyst, 1930, **55**, 187) found that this procedure was unnecessary, and that the addition of tartaric acid to the acid solution used in the copper pyridine thiocyanate test enabled the copper to be extracted by chloroform without interference from the iron. Ferrous salts, however, interfered with the reaction, and the method was not applicable in the presence of quantities of ferric iron greater than 40 mgrms.

I. Determination of Copper in the Presence of Iron.—The method which we suggest makes it possible to determine traces of copper in the presence of a large excess of iron without the necessity for the previous removal of the latter. This is effected by the addition of citric acid and ammonia to the solution containing the iron in the ferric condition. The reagent, a solution of sodium diethyldithiocarbamate, is then added, and the compound formed by the copper present with the reagent is extracted with carbon tetrachloride according to the

method suggested by Grendel (*loc. cit.*). Under these conditions no interference by the iron occurs.

Callan and Henderson (*loc. cit.*) found it necessary to precipitate the iron as ferric hydroxide before determining the copper. They state that no copper remains in the precipitate of ferric hydroxide. Our experiments show that this is not the case, and that an appreciable proportion of the copper remains in the precipitate.

Elvehjem and Lindow (*loc. cit.*) separated the copper from iron by precipitation with hydrogen sulphide, but we have found that even this treatment does not remove the whole of the copper from the iron.

PROCEDURE.—Dissolve 2 grms. of citric acid (A.R.) in the solution containing the iron in the ferric condition and not more than 0·1 mgrm. of copper in a volume not exceeding 50 c.c. Add ammonia until the *p*H of the solution is not less than 9, and dilute to 70 c.c. Add 10 c.c. of a 0·1 per cent. solution of sodium diethyldithiocarbamate, and extract immediately by shaking with four successive quantities of 2·5 c.c. of carbon tetrachloride added from a burette, running off the lower layer into a stoppered cylinder. If the final extract shows not more than the faintest trace of colour, determine the colour of the mixed carbon tetrachloride extracts in a 1 cm. all-glass cell in a Lovibond tintometer, and read off the amount of copper from a curve based on Table I, using only the yellow constituent of the colour. If the final carbon tetrachloride extract shows more than a trace of colour, continue the extraction with further quantities of 2·5 c.c. of carbon tetrachloride until no further colour is removed. Make up the volume of the mixed extracts to 20 c.c., determine the colour as before, and read off the amount of copper from a curve based on Table II. If the colour now exceeds 10 yellow units, too much copper has been taken, and the method must be repeated on a smaller quantity.

Standard colours containing known amounts of copper may be prepared by adding quantities of a solution containing 0·001 per cent. of copper to the alkaline solution in the separator after the copper previously present has been removed, and extracting in the manner described above. Comparisons may be made in a colorimeter or by direct comparison in tubes.

A control must be carried out in all cases with all the reagents, and the amount of copper found must be subtracted from the result.

NOTES ON THE METHOD.—All reagents should be as free from copper as possible in order to avoid a high blank subtraction.

Ferrous iron in quantities exceeding 1 mgrm. should be absent.

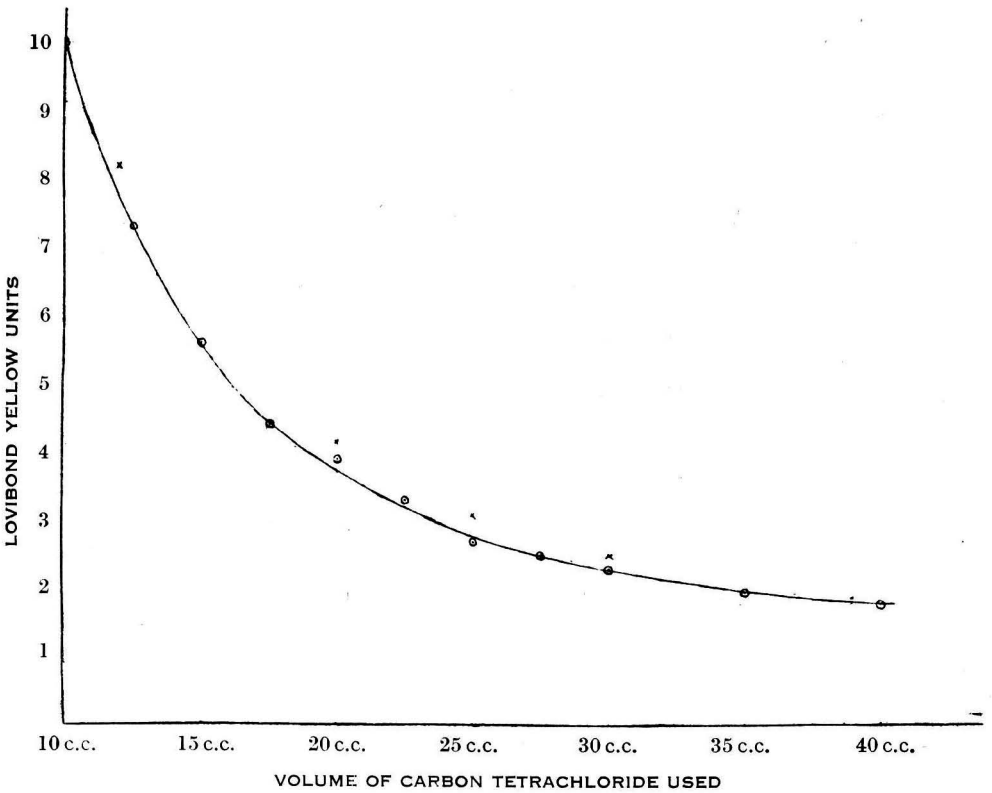
Two grms. of citric acid are sufficient for quantities of iron up to 0·1 grm. If the iron exceeds this amount, the citric acid must be increased proportionally.

Provided that the *p*H of the solution is not less than 9, a moderate excess of ammonia does not affect the results.

The following substances did not interfere with the method: Alkali metals, nitrates in amounts equivalent to 0·75 mgrm. of NO_3, sodium phosphate equivalent to 0·25 grm. of P_2O_5, calcium phosphate equivalent to 0·3 grm. of $Ca_3(PO_4)_2$. In the presence of calcium phosphate the *p*H should be approximately 9 and should not exceed that value, otherwise precipitation will occur. In the absence of iron, sulphurous acid, equivalent to 0·5 grm. of SO_2, did not interfere. Quantities as low

as 0·005 mgrm. of copper may be determined in the presence of as much as 0·25 grm. of iron, *i.e.* 0·002 per cent.

The colour is permanent for at least one hour; some fading occurs after four hours. The depth of the colour is not proportional to the concentration of copper; the relation is shown in the accompanying curve.



The points marked ⊙ on this curve were obtained by direct dilution with carbon tetrachloride of a solution giving 10 yellow units initially. The points marked * were obtained by extraction of known amounts of copper from the citrate solution. This shows that the dilution of a solution of the copper compound gives the same colour values as the same concentrations of copper when extracted directly, *e.g.* 0·05 mgrm. of copper was extracted with four quantities of 2·5 c.c. of carbon tetrachloride. The reading was 8·2 units. After dilution to 20 c.c. with carbon tetrachloride the reading was 3·1 units. The same quantity of copper was extracted with four quantities of 5 c.c. of carbon tetrachloride; the reading was again 3·1.

Curves were constructed by adding known amounts of copper to the copper-free ammoniacal citrate solutions containing the reagent. The following results were obtained:

TABLE I

Volume of carbon tetrachloride, 10 c.c.

Copper added Mgrm.	Colour Lovibond units Yellow
0·005	0·7
0·01	1·2
0·02	2·5
0·03	4·2
0·04	6·4
0·05	8·2

TABLE II

Volume of carbon tetrachloride, 20 c.c.

Copper added Mgrm.	Colour Lovibond units Yellow
0·05	3·1
0·06	4·2
0·07	5·1
0·08	6·3
0·09	7·4
0·10	8·3

These results were repeated in the presence of amounts of iron up to 0·25 grm. without altering the figures.

In order to confirm the fact that the presence of iron has no effect, quantities of ferric chloride were taken and the copper present was determined. Known amounts of copper were added, and the total copper was determined. The results are given in Table III.

TABLE III

Ferric chloride ($FeCl_3.6H_2O$) Grm.	Copper present Mgrm.	Copper added Mgrm.	Total copper found Mgrm.
0·5	0·022	0·010	0·031
0·5	0·022	0·020	0·041
0·6	0·055	0·030	0·088
0·6	0·055	0·005	0·059
1·0	0·008	0·010	0·018

ADSORPTION OF COPPER BY FERRIC HYDROXIDE.—The iron was precipitated from solutions of ferric chloride by the addition of ammonia. The precipitate was washed thoroughly, and the copper was determined both in the precipitate and in the filtrate.

Ferric chloride ($FeCl_3.6H_2O$) Grm.	Total copper present Mgrm.	Copper in precipitate Mgrm.	Copper in filtrate Mgrm.
1·0	0·022	0·014	0·007
0·6	0·055	0·050	0·006

PRECIPITATION OF COPPER BY HYDROGEN SULPHIDE.—(*a*) *In the absence of Iron.*—Fifty c.c. of a copper sulphate solution containing 0·5 mgrm. of copper were brought to *p*H 3·5 with dilute hydrochloric acid, the solution was boiled, and a current of hydrogen sulphide was then passed through it until it was cool. After filtration of the liquid through copper-free asbestos until colourless, the filtrate contained 0·022 mgrm. of copper.

(*b*) *In the presence of Iron.*—About 5 grms. of iron wire were dissolved in a slight excess of hydrochloric acid, the solution was diluted to about 100 c.c. with water and saturated with hydrogen sulphide, and the precipitate was filtered off through a copper-free sintered glass crucible. The filtrate was oxidised by boiling with a little nitric acid and evaporated to dryness. The copper found in the residue was 0·01 mgrm. per grm., and in a second experiment 0·02 mgrm. per grm. A further experiment was carried out in the same way, but with the solution kept at *p*H 3·5 during the precipitation. The copper found was 0·008 mgrm. per grm.

DETERMINATION OF COPPER IN THE PRESENCE OF OTHER METALS.—*Aluminium and Zinc.*—The same method works well in the presence of aluminium and zinc in quantities up to 0·2 grm. of aluminium or 0·1 grm. of zinc. In the absence of iron the aluminium or zinc may be dissolved in excess of sodium hydroxide solution with the addition of ammonia. On adding the reagent and extracting with carbon tetrachloride in the same way, results were obtained comparable with those obtained in the presence of iron, but with even larger quantities of aluminium and zinc (up to 0·5 grm. may be used).

Chromium.—The chromium must be in the chromic condition. If not, the solution must be reduced by the addition of sulphurous acid until no colour is given when a solution of diphenylamine in sulphuric acid is used as an external indicator. The solution is heated to boiling with 2 grms. of citric acid, and, after cooling, excess of ammonia is added. If the preliminary boiling is not carried out, chromium hydroxide is precipitated. The method may then be completed as described above. Amounts of chromium up to 0·2 grm. may be present.

Manganese.—If no more than a trace of iron is present, the copper may be determined in the presence of manganese (up to 0·2 grm.) by adding 2 grms. of citric acid and 5 c.c. of a 5 per cent. solution of sulphur dioxide, followed by excess of ammonia. A faint pink colour is extracted from solutions containing manganese, but the copper is still proportional to the yellow constituent in the Lovibond tintometer.

Tin.—In the absence of iron, traces of copper may be determined in the presence of stannic salts by the addition of an excess of sodium hydroxide and ammonia in the same way as described under aluminium and zinc.

Our thanks are due to Messrs. Allen & Hanburys, in whose laboratories this work was carried out.

The Determination of Silicon in Aluminium

By L. H. CALLENDAR, Ph.D., F.I.C., A.R.C.S.

In analysing commercial aluminium it is customary to determine silicon and iron only, and not to determine other impurities, when, as is usually the case, they are present in quantities of less than 0·01 per cent. Of these standard determinations that of silicon is the more important, not only because it occupies most of the time of the analyst concerned with aluminium, but also because the solubility of silicon in aluminium (iron is practically insoluble) causes variations in the mechanical, physical and electrical properties of the metal. More recently the extensive use of aluminium-silicon alloys has added further interest to the question.

As the result of experience in the metallurgical laboratories of the British Aluminium Company, it has been found that, for accurate analysis, the best results are obtained by a method in which the metal is dissolved in soda solution, and the silica then separated by acid; the older processes in which the metal is dissolved directly in mixed acids give low results, owing to the loss of volatile silicon compounds during solution of the metal.

In this paper it is proposed first to examine the main errors which are liable to occur in all the commonly used methods for the determination of silicon in aluminium, to show by experimental results the conditions under which these errors can be reduced to a minimum, then to give the experimental details of the procedures which have been found best for the four principal methods, and also to provide some guidance as to the choice of method for accurate and routine analyses of pure metal and aluminium-silicon alloys.

Conditions of Ignition for Obtaining Non-hygroscopic Silica Residues.—The most common causes of high results in silicon analysis are incomplete ignition of the silica residue and absorption of moisture by the residue before and during the weighing operations. As the available information in the literature was contradictory and inexact, experiments were carried out to determine the best conditions for the ignition of silica residues obtained during the analysis of aluminium and aluminium-silicon alloys.

The results in Table I are for silica residues from an aluminium-silicon alloy analysed by the soda method (for full experimental details, see Method A, p. 506), and the results in Table II are those obtained with mixed residues from commercial aluminium analysed by the mixed acid process (see Method B). The ignitions were carried out in porcelain crucibles, a blank crucible being heated alongside to check any changes in weight of the crucible. The temperature of the muffle furnace used was determined by means of thermo-couples inserted alongside the crucibles.

TABLE I

TEMPERATURE OF IGNITION AND MOISTURE-ABSORPTION OF SILICA RESIDUES

Exp. No.	Temperature and duration of ignition ° C.	First weight of ignited residue Grm.	Moisture-absorption after standing 3 days in open air Grm.	Loss of weight on 2nd ignition at 900° C. for 30 mins. Grm.	Moisture-absorption after again standing in air for 18 hours
970	400–600° Rising in	0·1177	0·0147	0·0199	Nil
971	30 min.	0·1136	0·0140	0·0187	Nil
972	600–700° Rising in	0·1095	0·0020	0·0096	Nil
973	30 mins.	0·1167	0·0103	0·0160	Nil
974	700–800° Rising in	0·1143	0·0101	0·0153	Nil
975	30 mins.	0·1163	0·0072	0·0146	Nil
965	800–1000° Rising in	0·1123	Nil	0·0004	Nil
977	40 mins.	0·1101	Nil	0·0021	Nil

TABLE II

INCOMPLETE IGNITION OF SILICA RESIDUES

Exp. No.	Temperature and duration of ignition	Weight after ignition Grm.	Re-ignition temperature ° C.	Weight after re-ignition Grm.	Loss per cent.
2634	770–800 °C. for	0·0698	900°	0·0646	7·5
2634	about 30 mins.	0·0718	for 1 hour	0·0668	7·0
2632		0·0414		0·0374	9·7
2632		0·0414		0·0376	9·2
2635		0·1010		0·0964	4·7
2637		0·0992		0·0918	7·5
2638		0·1006		0·0922	8·4

As the results given in Tables I and II are evidently of the first importance for obtaining accurate results in the determination of silicon, some confirmatory experiments were carried out. For these experiments some 60 silica residues were collected from routine analyses of commercial aluminium by the mixed acid process, and were well mixed together, and about 0·1 grm. of the mixture was weighed out into each of 4 platinum crucibles. In a further series the residues from a number of analyses of aluminium-silicon alloy by the soda process were also collected and mixed, and they were weighed into another series of platinum crucibles; they were then ignited for 1 hour at 850° to 950° C., exposed to the air for 2 hours, and weighed. A comparison of the residues from the two processes showed that the amounts of moisture absorbed by the ignited residues ranged from *nil* to 0·0003 grm.

In actual practice it is unlikely that the silica residues would be exposed to the air for as long as half-an-hour before and during weighing.

The results given in Tables I and II indicate that these silica residues require to be heated at 900° C. for about 1 hour to ensure their dehydration and to render them non-hygroscopic. If the residues are heated in porcelain crucibles the temperature of the muffle furnace should not be allowed to rise above 1000° C., as small residues are liable to become fused into the bottom of even the best porcelain crucibles. Some of the results indicated that there is a slight tendency for residues from the mixed acid routine process to absorb moisture, even after 1 hour's ignition at 900° C. This is due to the presence in these residues of 6 to 8 per cent. of alumina (about 5 times as much alumina as is contained in the residues from the soda method), which is more difficult to render non-hygroscopic than the silica itself. As the moisture absorbed in these experiments amounts to only 0·2 per cent. of the weight taken, the error introduced would obviously be quite negligible in the routine analysis of commercial aluminium, in which the average silicon content might be of the order of 0·20 per cent. For the most accurate analysis, however, especially with large silica residues, it is advisable after 1 hour's ignition at 900° C., to re-ignite the residue for half-an-hour, and, if the further loss of weight is then inappreciable, the amount of silicon in the residue may be determined by treatment with hydrofluoric acid.

Use of Hydrofluoric Acid Method for Determining Silica in Residues.—Although, in general, this process is well known, it is advisable to point out certain errors to which it has been found liable in the particular case of the determination of silica in siliceous residues from aluminium.

The usual procedure is as follows:—The siliceous residue left after ignition in a platinum crucible is treated with a few drops of concentrated sulphuric acid, and then with 1 to 2 c.c. of hydrofluoric acid. The crucible is very carefully warmed until all the acid has been expelled, after which it is ignited for a few minutes and allowed to cool, and the process is repeated until a constant weight is obtained. The loss of weight is taken as the silica in the residue.

The chief source of error is the presence of alumina in the residue. In the "fuming" process this alumina appears to be partly converted into aluminium sulphate, which is not completely decomposed by the subsequent ignition; this makes the silicon results too low. It was found from a number of experiments that to ensure decomposition into Al_2O_3, it is necessary to heat the residue at 1000° C. for about 10 minutes, after the treatment with hydrofluoric acid.

Errors due to impurities in the hydrofluoric acid itself can be avoided by making a simultaneous blank determination. Residues contaminated with vanadium oxide from a vanadium aluminium alloy must be heated with hydrofluoric acid and freed from sulphuric acid on the hot plate before being heated over a flame. Residues which are brown in colour, owing to the presence of silicon, require special treatment.

Treatment of Brown Siliceous Residues from Acid Processes.—In the method proposed by Regelsberger, in 1891, the silica and silicon are determined separately by a double process of heating, first with hydrofluoric and sulphuric

acids (the loss of weight being taken as equal to the silica in the original residue) and then with a mixture of hydrofluoric and nitric acids, the loss of weight obtained being assumed to be equivalent to the silicon in the original residue. This process has been advocated by W. H. Withey (*J. Inst. Metals*, 1916, **15**, 207), and by the American Society for Testing Materials for the determination of graphitic silicon in aluminium; further, it has been used by Honigschmidt in his attempts to prove the existence of silicon sub-oxides (*Ber.*, 1909, **118**, 289), and it is included in many modern textbooks. Experimental results obtained at the Warrington laboratory tend to show that this process is not only inaccurate, but also quite useless for the determination of silica or silicon in a mixture of the two. The cause of the inaccuracy of the process is that in the first heating with acid and ignition part of the silicon is oxidised to silica, and in subsequent repetitions of the process this silica is volatilised by the hydrofluoric acid, and so on until all the silicon is volatilised, without the use of nitric acid at all; moreover, according to Manchot (*Ber.*, 1921, **54**, 3107), silicon itself is directly attacked by hydrofluoric acid *plus* sulphuric acid, and some may be lost as silicon fluoride.

This loss of silicon by heating with hydrofluoric acid *plus* sulphuric acid alone is illustrated by the results given in Table III; these results are merely typical of many obtained in this laboratory.

For the first experiments pure silicon was prepared from crystalline material by the N.P.L. method (N. P. Tucker, *J. Iron Steel Inst.*, 1927, **115**, 142); the results of the first four treatments with two samples of this material with hydrofluoric acid *plus* sulphuric acid are shown in the table; after ten further treatments the material continued to lose weight at much the same rate. A sample of so-called pure amorphous silicon, obtained from a well-known supplier, was treated in the same way; after five heatings this material ceased to lose weight, and the brown residue was found to consist only of iron oxide and alumina, all the silicon originally present having been expelled. The second series of results in Table III was obtained with dark brown siliceous residues from low-purity aluminium; after 2 to 3 treatments these residues became colourless, and the residual powder was pure alumina. It should be added that no nitric acid could be detected in the hydrofluoric and sulphuric acids used in all our experiments.

TABLE III

LOSS OF SILICON ON TREATMENT WITH HYDROFLUORIC ACID

Sample	Weight	First loss	Second loss	Third loss	Fourth loss	
	Grm.	Grm.	Grm.	Grm.	Grm.	
Pure cryst. silicon	0·1000	0·0021	0·0010	0·0010	0·0029	
	0·0657	0·0018	0·0030	0·0040	0·0018	
Brown siliceous residues from aluminium	0·0134	0·0110	0·0014	Nil		Residues quite white, only Al_2O_3 left
	0·0127	0·0103	0·0022	Nil		
	0·0196	0·0146	0·0015	0·0014		

From these results it is clear that Regelberger's method is of no use whatever for the determination of silicon and silica in a mixture of the two. (R. L. Johnston, *Chemist-Analyst*, 1924, **41**, 9; D. von Prettner, *Chem. Ztg.*, 1927, 261.)

A satisfactory procedure for the treatment of siliceous residues containing silicon was proposed by Hunt, Clapp and Handy in 1892 (*J. Anal. Appl. Chem.*, 1892, **6**, No. 1; see also H. J. Williams, *Trans. Amer. Inst. Min. Eng.*, 1888, **17**, 542). They suggested that the brown residues should be fused with sodium carbonate, and that the silicon, being oxidised to silica, should then be separated by treatment with excess of acid as usual. A simpler and more convenient procedure is to treat the residues by the soda method (Method A).

If the aluminium metal is known to contain much free silicon, half the time of the analysis may be saved by dissolving the metal in sodium hydroxide solution instead of acid at the outset and proceeding by the usual soda method.

Impurities in Siliceous Residues.—As has been pointed out, the siliceous residues obtained from aluminium by any of the methods of separation discussed in this paper contain variable amounts of impurities (mainly Al_2O_3). The percentage of impurities varies from about 1 per cent. for residues from 10 per cent. silicon alloys, to 6–10 per cent. for residues from commercial metal, and it cannot be reduced in either case without seriously increasing the loss of silica in the filtrates and wash-water.

Loss of Silica in the Filtrates.—The question of the loss of silica in the filtrates in different methods of determining silicon in iron and steel and ferro-silicon has frequently been investigated, more particularly by Stadeler (*Stahl und Eisen*, 1927, **47**, 966; *Archiv für das Eisenhüttenwesen*, 1929, **2**, 425), who gives many hundreds of results obtained from eleven different laboratories by means of sixteen different methods of analysis. The results given here are some of those obtained in the determination of silicon in aluminium by the mixed acid process and by the soda process.

Table IV

Analysis of H.P. Cast Metal by Mixed Acid Process

Exp. No.	Material	Residue Grm.	Silica by treatment with HF Grm.	Residue from filtrate Grm.	Silica Grm.	Second filtrate Grm.	Silica Grm.	Total silica Grm.	Nett silicon Per Cent.
1100–1	10 grms. of Hoope's American	0·0117	0·0109	0·0012	0·0010	Mean nett SiO_2		0·0121	0·0544
1102–3	metal (duplicates)	0·0114	0·0104	0·0017	0·0015	=0·0002		0·0121	
1104–5	Blanks on	0·0001	0·0001	0·0003	0·0002	Nil		0·0003	Blank SiO_2
1106–7	reagents	0·0002	0·0002	0·0005	0·0004			0·0006	mean=0·00045
1042	5 grms. of Hoope's	0·0052	0·0047	Approximate analysis, neglecting filtrate losses and blanks.					0·045
1043	American metal	0·0052	0·0049						
1070	10 grms. of Foyer's	0·0208	0·0185	0·0020	0·0010	0·0008	0·0006	0·0201	0·0888
1071	99·8 per cent. metal	0·0202	0·0183	0·0021	0·0011	0·0008	0·0003	0·0197	
1075	Blanks on	0·0009	0·0007	0·0008	0·0002	0·0006	0·0003	0·0012	Mean blank
1076	reagents	0·0013	0·0006	0·0007	Nil	0·0003	Nil	0·0006	SiO_2=0·0009
1044	5 grms. of Foyer's	0·0092	0·0090	Routine analysis correcting for filtrate losses by the use of the factor 48·5 (see p. 505)					0·088
1045	99·8 per cent. metal	0·0096	0·0091						

The first results given in Table IV show typical filtrate losses found by the mixed acid process in the analysis of high-purity cast metal, the analysis being carried out according to the details given in Method B; in each case the residues obtained were quite white, and the silica was determined directly by heating them with hydrofluoric acid. The experiments 1042–3 show the large error introduced into the results by neglecting the filtrate losses.

Results showing typical filtrate losses with the soda method are given in Table V; these are results of duplicate determinations on commercial metal and aluminium-silicon alloys. From the mean of these filtrate losses a factor can be calculated which may be used in routine analysis to avoid the lengthy re-evaporation of the filtrates; this factor is given in the last column of the table. In these experiments the mean filtrate loss works out at 3·24 per cent.

TABLE V

STANDARD SODA METHOD

CORRECTIONS FOR NORMAL SILICON LOSS IN FILTRATION

Exp. No.	Weight of metal taken Grm.	Silica in residue A after treatment with HF. Figure corrected for SiO_2 in blank Grm.	Filtrate silica 1st & 2nd filtrate residues corrected, etc. Grm.	Total silica from metal Grm.	Filtrate loss Per Cent.	Corrected factor ($\times SiO_2$ in 1st residue, A=silicon in metal) Per Cent.
1160–1	1	0·0038	0·0001	0·0039	2·6	48·3
1162–3	,,	0·0053	0·0002	0·0055	3·6	48·8
1110–1	,,	0·0070	0·0003	0·0073	4·1	49·0
1009–10	,,	0·0099	0·0003	0·0102	2·9	48·4
1166–7	,,	0·0121	0·0004	0·0125	3·2	48·5
1168–9	,,	0·0163	0·0006	0·0169	3·5	48·7
1117–8	,,	0·0228	0·0010	0·0238	4·2	49·1
1013–4	,,	0·0590	0·0024	0·0614	3·9	48·9
1015–6	,,	0·1151	0·0031	0·1182	2·6	48·3
940–1	0·5	0·0690	0·0021	0·0711	3·0	96·8
1130–1	,,	0·0975	0·0029	0·1005	2·9	96·8
942–3	,,	0·1206	0·0029	0·1235	2·4	96·2

Mean factor for 1 grm. of metal = 48·5

It has often been stated that filtrate losses can be prevented or greatly reduced by the use of pulp-pad filters; the experimental results given below show, however, that there is little difference between the filtrate losses of silica obtained with pulp-pad filters and the losses obtained with papers of good quality. The results of a comparison between a loose pulp pad (for this the pulp was merely poured into the funnel without any pressing down), a tight pad well pressed down, and Schleicher and Schüll papers of four different textures are given in Table VI. The results are the mean of duplicate determinations.

TABLE VI

COMPARISON OF FILTER PAPERS AND PULP PADS

Exp.	Filter medium	Total silica Grm.	Filtrate loss Per Cent.
12–13	Pulp pad, loose	0·0717	4·0
10–11	Pulp pad, tight	0·0717	3·6
14–15	Paper coarse S. & S. 589, black	0·0721	3·5
16–17	Paper medium 589, white	0·0716	3·0
18–19	Paper fine 589, blue	0·0719	3·1

The results in Table VI seem to indicate a slight advantage in the use of medium filter paper for accurate work; for routine work the pulp pads offer considerable advantages, as they are easier to wash, and tend to accelerate the filtration.

Large variations in the amount of filtrate loss are primarily due to the *time* taken in boiling with water after the first dehydration of the silica with sulphuric acid. By varying this time from 1 minute to 30 minutes the filtrate loss has been found to vary from 1 to 5 per cent., while at the same time the alumina-content of a large residue may vary from 5 to 10 per cent. The results of a large number of experiments have shown that boiling for about 15 minutes gives a nearly uniform filtrate loss of about 3 per cent. (with Schleicher and Schüll medium papers), with a residue containing minimum amounts of alumina. The actual time, beyond 5 to 10 minutes, during which the residue is heated after being evaporated with sulphuric acid until fumes appear, does not appear to influence the filtrate losses, but very prolonged treatment increases the amount of alumina in the residue, and is, therefore, disadvantageous.

EXPERIMENTAL DETAILS OF METHODS.—The experimental details of the four principal methods which have been used for the determination of silicon in aluminium are those which have been found to be best from experience in a laboratory where some 10,000 silicon determinations on aluminium and its alloys are carried out every year.

METHOD A—SODA METHOD

The metal is dissolved in 10 per cent. caustic soda solution in a covered nickel crucible, and the liquid is boiled, diluted and poured into excess of 60 per cent. sulphuric acid. It is then evaporated until fumes appear and diluted, and the silica is filtered off and determined.

The quantities of alkali, acid, etc., required for different classes of metal are given in the Table VII.

TABLE VII

QUANTITIES USED IN SODA METHOD FOR SILICON DETERMINATION

Metal with silicon content Per Cent.	Weight of metal Grms.	Volume of 10 per cent. soda solution c.c.	Volume of 60 per cent. sulphuric acid c.c.
0·05 to 0·15	5	100*	180
0·15 to 0·50	2	50	100
0·4 to 5	1	30	60
2 to 15	0·5	20	35
12 to 25	0·25	20	35

* Nickel crucibles of one-litre capacity may be used for metal of high purity, though the silicon in this class of metal is more conveniently determined by the sulpho-nitric acid process (Method C).

EXPERIMENTAL DETAILS.—Weigh out 1 grm. of millings (*e.g.* of metal containing about 1 per cent. of silicon) into a 200-c.c. nickel crucible, add 30 c.c. of freshly-prepared 10 per cent. sodium hydroxide solution and cover the crucible with the lid. When nearly all the metal has dissolved, wash down the lid and sides of the crucible with a very little hot water, replace the lid, and boil the liquid briskly on the hot plate for about 10 minutes, just avoiding evaporation to complete dryness. Remove the crucible from the plate, wash down the lid and sides, dilute the liquid to about 40 c.c., boil until most of the residue is detached from the bottom of the crucible; then transfer the contents to a 400-c.c. shallow beaker, already containing 55 c.c. of 60 per cent. sulphuric acid, and add the aluminate solution to the acid, meanwhile rotating the beaker.

Wash out the crucible with 5 c.c. of 60 per cent. sulphuric acid, and then with hot water, finally removing any silica particles adhering to the side and lid by means of a rod tipped with rubber. Cover the beaker with a clock-glass and evaporate the liquid rapidly on the hot plate, carefully avoiding spurting; heat until strong fumes appear, and continue the heating for 15 minutes.

Remove the beaker from the plate, allow the residue to cool a little, add from a wash-bottle (keeping the cover-glass still on the beaker) a fine stream of cold water (just a few c.c. to break up the cake), and then wash down the cover-glass and sides of the beaker with cold water. Add about 150 c.c. of hot water, stir with a rod tipped with rubber to detach the cake and prevent bumping, heat to boiling, and boil gently for 15 minutes. Filter on a Schleicher and Schüll medium paper (589 white band) or on a pulp pad. Wash out the beaker with hot water, remove any adhering silica, and then wash the filter pad twice with hot water.

Wash the residue on the filter three times with hot dilute (1:3) hydrochloric acid, allowing the filter to drain after each addition of acid, and then wash 8 to 10 times with hot water, testing the final filtrate for chlorides with silver nitrate solution. Transfer the paper or pad to a platinum crucible, dry on the hot plate, then transfer to a muffle furnace, ignite for 1 hour at 900° C., cool for 1 hour in a desiccator, and weigh. Re-ignite for 15 minutes over a blast lamp, cool and weigh. If this second loss of weight is inappreciable, as it usually is, the residue is now ready for heating with hydrofluoric acid.

To the platinum crucible add 4 drops of concentrated sulphuric acid and about 1 c.c. of hydrofluoric acid, replace the lid and evaporate the liquid carefully over a very low flame in a fume-cupboard. When no more fumes are evolved, ignite the crucible and its contents over a blast-lamp for 10 minutes, cool and weigh. Repeat the treatment with hydrofluoric acid, adding this time 2 drops of sulphuric acid and 0·5 c.c. of hydrofluoric acid, evaporate, ignite, cool and weigh. If the change of weight is inappreciable, further treatment with hydrofluoric acid is unnecessary. The loss of weight represents the pure silica in the residue, after a correction has been made for impurities in the hydrofluoric and sulphuric acids.

For accurate analysis, blank determinations must always be made. The filtrates from the first filtration, which contain about 3 per cent. of the total silica, must be evaporated again after the addition of 10 c.c. of 60 per cent. sulphuric acid; the filtrates obtained after this treatment may also be treated to recover any silica they may contain, but usually the amount recovered here is not

appreciably greater than that found in the blank determination. The silica recovered from the filtrates may be added to the main bulk, and submitted with it to the treatment with hydrofluoric acid. (Total silica 0·4672 = silicon.)

ROUTINE ANALYSIS OF METAL OF KNOWN ORIGIN.—In this case the analysis can be greatly shortened by omitting the re-ignition of the silica residue, and also the heating with hydrofluoric acid, the correction to the results to allow for these omissions being found by re-igniting a number of residues and then heating them with hydrofluoric acid (in the routine analysis of 10 per cent. silicon alloy I have used a correction figure of 0·0015 grm.). The analysis can be further shortened by omitting the recovery of silica from the filtrates and making an allowance for this by calculating the SiO_2 to Si by the corrected factor 0·485, obtained as a mean of the results in Table V.

NOTES.—The 10 per cent. sodium hydroxide solution should be freshly prepared in a nickel basin or crucible. A nickel rod may be used for mixing the solution, which should be measured out in a nickel cylinder, and the reaction crucible and its lid should be handled with nickel tongs.

With silicon-aluminium alloys (*e.g.* the common 10 to 14 per cent. alloys) after evaporation of the soda solution the residue in the crucible should contain no visible brown particles; if, however, it is brownish, the soda should be diluted with about 10 c.c. of hot water, and boiled again for a few minutes to complete the conversion of the silicon into silica.

After having cooled down somewhat after the heating with sulphuric acid, the contents of the beaker should be diluted with a little *cold* water, as this throws out the silica in a granular form suitable for filtration, and also avoids spurting.

This soda method is especially suitable for the accurate or routine analysis of low-purity metal and aluminium-silicon alloys.

METHOD B—MIXED ACID PROCESS

The metal is dissolved in a dilute acid mixture ($HCl+HNO_3+H_2SO_4$). The liquid is evaporated until it fumes strongly, and the silica is separated as usual. The residue may then be fused with fusion mixture ($Na_2CO_3+K_2CO_3$), the fused mass is treated with excess of acid, the solution is evaporated until fumes appear, and the silica is separated as before. In either case the final residue is determined by evaporation with hydrofluoric acid (*cf.* F. Regelsberger, *Z. angew. Chem.*, 1891, **1**, 442; *Amer. Soc. Test. Mat., Tentative Standards*, 1928, p. 782).

The acid mixture which has been found most convenient for routine determinations of silicon is as follows:—

675 c.c.	of sulphuric acid of sp.gr.,	1·84
338 c.c.	of nitric acid of ,,	1·42
338 c.c.	of hydrochloric acid of ,,	1·16
3150 c.c.	of distilled water.	

EXPERIMENTAL DETAILS (FOR COMMERCIAL METAL).—Weigh out 1 grm. of millings into a 400-c.c. shallow beaker, add 35 c.c. of acid mixture, and cover with a clock-glass. Warm on the hot plate until the action starts, remove and let the action continue until the metal is practically dissolved. Wash down the cover glass and sides of the beaker with hot water, transfer the beaker to the hot

plate and evaporate until fuming begins, care being taken to avoid spurting. Transfer the beaker to the cooler part of the plate and allow the acid to fume strongly for 10 to 15 minutes.

Then proceed exactly as with the soda method (Method A), filtering off the silica on a paper-pulp pad. After washing as before, dry the pulp pad by means of suction with the aid of the filter pump, transfer the pad to a porcelain crucible by means of tongs, removing all traces of silica adhering to the funnel with moistened filter paper, which is added to the main residue in the crucible.

Ignite in a muffle furnace and burn off the filter paper, allow the crucible to cool, transfer the residue to a nickel crucible, and mix it with eight times its amount of pure fusion mixture. Heat the mixture to fusion and continue heating until the liquid appears fairly transparent and clear. Cool quickly in cold water to crack the cake, transfer this to a 400-c.c. beaker containing a little hot water, and rinse the nickel crucible into the beaker.

Add 60 per cent. sulphuric acid gradually to the contents of the beaker, until acid to litmus, and finally add about 20 c.c. in excess. Evaporate until the acid fumes strongly, take up the residue, filter, and wash as in the soda method. Ignite the final residue to constant weight at 900° C., and determine the silica by the usual treatment with hydrofluoric acid.

This method is unsuitable for analyses where a high order of accuracy is imperative, owing to the loss of volatile silicon compounds during the solution of the metal.* It has the further disadvantages of taking about twice as long as the soda method, and of being subject to double filtration losses.

ROUTINE ANALYSIS.—The mixed acid process is convenient for the routine determination of silicon in commercial aluminium. By the use of the modified factor referred to above the process can be greatly shortened and made sufficiently accurate for industrial purposes, when the conditions under which the metal is produced are more or less constant, as, of course, they usually are in any large-scale production.

For routine analysis of commercial cast metal, the first silica residue is ignited for about 1 hour at 850–950° C.; after cooling in a desiccator, it is weighed, and the weight obtained is multiplied by the empirical laboratory factor to obtain the percentage of silicon. I have found in practice that a factor of 48 for the routine mixed acid process gives results which agree well with those obtained by the soda method with pure cast metal.

It is, however, advisable for other laboratories wishing to use the mixed acid process for routine analysis, to determine their own factors by comparing the results of, say, six duplicate analyses by different operators of a dozen different samples of metal by the mixed acid process with accurate analyses of the same samples by the soda method. Even then, the routine process is not suitable for the determination of silicon in metal which has been heat-treated at a low

* The experimental evidence on which this statement is based forms part of the subject-matter of another paper to be published shortly. In the meantime it may be said that the evidence of several hundred experiments shows that the mixed acid process almost always gives low results, as compared with the soda method, and that this difference has been found to be due solely to the loss of volatile silicon compounds.

temperature (300° C.) so as to throw most of the silicon out of solution, or at a high temperature (550° C.), so as to bring the silicon into solid solution. Such metal should be analysed by the soda method or by the sulpho-nitric acid process, with re-annealing if necessary.

Method C—Sulpho-Nitric Acid Method

The metal is annealed for 2 to 12 hours at 570° C., and then quenched in cold water. It is dissolved in a mixture of concentrated nitric acid and 60 per cent. sulphuric acid. After solution, the silica is separated by the usual method, and, after ignition, the white residue is treated with hydrofluoric acid to determine the silica.

Experimental Details.*—Dissolve 5 grms. of millings in duplicate in 1500-c.c. shallow beakers in 150 c.c. of a mixture of sulphuric and nitric acids (60 c.c. of 60 per cent. sulphuric + 40 c.c. of concentrated nitric acid). Evaporate down carefully to avoid spurting. Heat in the usual way until fumes appear.

Then remove the beakers from the plate and allow them to cool for 5 to 10 minutes before diluting the liquid very carefully with a thin stream of water from the wash-bottle. Dilute to about 700 c.c., filter on a Schleicher and Schüll paper, No. 589/2, and wash the residues as usual. Dry and ignite the residues in platinum crucibles at 900° C. until constant in weight. Heat with hydrofluoric acid as in the soda method to determine the silica.

Collect the filtrates, add 10 c.c. of 60 per cent. sulphuric acid, heat until the acid fumes strongly, dilute, boil, filter, ignite, and treat with hydrofluoric acid. Blank determinations should be made at the same time.

$$\begin{aligned} \text{Silicon} &= \text{SiO}_2 \text{ in 1st residue} \times 0{\cdot}485 \quad \ldots\ldots\ldots\ldots \quad (1) \\ &= \text{1st+2nd} \quad \text{,,} \quad \times 0{\cdot}470 \quad \ldots\ldots\ldots\ldots \quad (2) \\ &= \text{1st+2nd+3rd} \text{,,} \quad \times 0{\cdot}4672 \ldots\ldots\ldots\ldots \quad (3) \end{aligned}$$

By applying the factor 0·47 to the weight of the silica found in the first and second residues, the results obtained by this method agree very closely with those obtained by the soda method.

This sulpho-nitric acid process is somewhat more convenient than the soda process for the determination of silicon in high-purity metal. For routine analysis of commercial metal, it is not so safe in the hands of less experienced workers as the mixed acid process, owing to the high concentration of acid used.

Method D—Sulphuric Acid Process

The metal is dissolved in sulphuric acid (sp.gr. 1·6), the solution is filtered without being heated until it fumes, and the siliceous residue is ignited directly and weighed. (*Cf.* F. Ahrens, *Chem. Tech. Analyses*, 1901.)

Experimental Details.—In the case of commercial metal, 3 grms. of the sample are weighed out into a 500-c.c. flask fitted with a wide glass tube to act as a reflux condenser, and 100 c.c. of sulphuric acid (sp.gr. 1·6) are added. The flask is warmed, gently at first, and then more strongly, until all the metal is in

* For high-purity metal, annealing is unnecessary.

solution. After the solution has cooled somewhat, about 350 c.c. of warm water are added, the liquid is filtered on a pulp pad, and the residue is washed with boiling water. The pad is transferred from the filter to a porcelain crucible, dried, ignited at 900° C. for 1 hour, cooled and weighed.

The weight of residue, multiplied by a factor found as for the mixed acid process (Method B), gives the silicon content of the metal.

COMMENTS.—This method, D, is suitable only for routine analysis. It is considerably more rapid than any of the other methods, as the lengthy heating with acid is avoided, silicon and silica being practically insoluble in sulphuric acid of sp.gr. 1·6.

The work here described was carried out in the Research Laboratories of the British Aluminium Company at Warrington. The author wishes to acknowledge his indebtedness to Dr. A. G. C. Gwyer and to the British Aluminium Company for permission to publish the paper.

Observations on the Use of Adsorption Indicators in Titrations of Halides of Limited or Reversible Ionisation

BY A. J. BERRY, M.A.

IT has been shown by Berry and Durrant (ANALYST, 1930, **55**, 613) that phenosafranine* and tartrazine are very satisfactory adsorption indicators for such volumetric determinations involving the use of silver nitrate as have to be carried out in acid solution. Subsequent experiments have amply justified their use, and, although experiments have been made with many other dyestuffs, none has been found to be so good for this purpose, except a pyrazelene, described as *pyrazolone jaune* (Produits chimiques de Saint Denis), which behaved exactly like tartrazine. These indicators may be safely used in the presence of a concentration of free nitric acid of the order of normal. Tartrazine may also be used in the presence of dilute sulphuric acid, but phenosafranine should not be used with this acid, on account of the bleaching action which the acid exerts upon the blue silver derivative of this dyestuff.

No difficulties were encountered in any titrations of halides in which the ionisation was straightforward. When, however, experiments were made with compounds in which the ionisation was known to be limited or reversible, irregularities were to be expected, and were indeed observed. In this connection, two rather different types of limited ionisation have to be considered, *viz.* that of compounds such as chloropentammine cobaltic chloride, $[ClCo(NH_3)_5]Cl_2$, in

* Regarding phenosafranine, it should be mentioned that this dyestuff had been used prior to the publication of Berry and Durrant by H. M. Weir (*Dissertation*, München, 1926). The authors were ignorant of Weir's publication, and regret that it was overlooked.

which two-thirds of the chlorine is ionisable, and that of weak electrolytes, such as the mercuric and thallic halides. In the former, if the co-ordinated complex ion is fairly stable, it is a simple matter to realise the ionisable chlorine by titration with silver nitrate (with phenosafranine as indicator) with a fair degree of accuracy, whereas in the latter the action of the indicator is impeded in such a way as to make the determination of the end-point very difficult, or altogether impossible. The following results may be quoted by way of illustration:

1. (*a*) CHLOROPENTAMMINE COBALTIC CHLORIDE.—Fifty c.c. of a solution of this salt containing 3·22 grms. per litre required 19·45 c.c. of a solution of silver nitrate containing 11·72 grms. per litre, phenosafranine being used as indicator. The percentage of ionisable chlorine is, therefore, 28·9 per cent. To determine the total chlorine, 50 c.c. of this solution were reduced by shaking with a 2·5 per cent. zinc amalgam in presence of very dilute sulphuric acid. The solution required 28·0 c.c. of silver nitrate, with *pyrazolone jaune* as indicator, from which it follows that the total chlorine is 42·7 per cent.

In another experiment the total chlorine was determined by reducing 0·727 grm. of the salt dissolved in 100 c.c. of *N* sulphuric acid by shaking with 2·5 per cent. zinc amalgam. The liquid was then diluted to 250 c.c. with water. Twenty c.c. of silver nitrate (11·72 grms. per litre) required 39·8 c.c. of the reduced cobalt solution, tartrazine being used as indicator. The total chlorine was, therefore, found to be 42·3 per cent. The values calculated from the formula are: 28·3 per cent. for the ionisable chlorine, and 42·5 per cent. for the total chlorine.

Various other experiments were made on this salt, with precisely similar results. It may be noted that phenosafranine is particularly well suited for titrations of the ionisable chlorine, as the end-point is easy to recognise in the presence of the purple-red colour of the solution. The value of liquid amalgams, introduced by Nakazono and Someya for effecting reductions in volumetric analysis, has been amply verified by Russell (*e.g. J. Soc. Chem. Ind.*, 1926, **45**, 57T.), and I have found it to be very convenient for these and for other similar experiments. When a solution of chloropentammine cobaltic chloride is kept for some time, it undergoes slow hydrolysis, with formation of aquopentammine cobaltic chloride, in which all the chlorine is in the ionic condition. This hydrolysis can be followed by titration with silver nitrate, phenosafranine being used as the indicator. It was found that in a solution which had been kept for three weeks at the ordinary temperature, the ionisable chlorine had increased by over 25 per cent.

$$\overset{++--}{[ClCo(NH_3)_5]Cl_2} + H_2O = \overset{+++---}{[(H_2O)Co(NH_3)_5]Cl_3}.$$

(*b*) CHROMIC CHLORIDE.—It is well known that the three modifications of the hexahydrate of this salt differ not only in colour, but also in their behaviour towards silver ions. In the violet form all the chlorine is in the ionic condition, in the light green form (Bjerrum's salt) this amounts to two-thirds, whilst in the dark green form only one-third of the chlorine is in this condition. The rapidity of the transformations in aqueous solution, however, renders verification of these phenomena by analytical methods exceedingly difficult. The investigations of

Weinland and Koch (*Z. anorg. Chem.*, 1904, **39**, 296) and of Olie (*ibid.*, 1907, **52**, 48) have shown that the presence of strong acids exerts an impeding action on the transformation of the green salt into the violet isomer, and the following attempt to verify this phenomenon by titration with silver nitrate, with the aid of an adsorption indicator, although only partly successful, may be of interest.

Anhydrous chromic chloride cannot be dissolved directly by water, but traces of reducing agents which produce some chromous chloride enable the salt to dissolve easily (Drucker, *Z. physikal. Chem.*, 1901, **36**, 173). After various methods had been tried, it was found most convenient to dissolve the salt by shaking with 2·5 per cent. zinc amalgam and dilute acetic acid. The liquid thus obtained was left exposed to the air for a short time to allow any chromous salt to be re-oxidised to the chromic condition. It was then divided into two equal portions, one of which was diluted with four times its volume of water, and the other with four times its volume of normal nitric acid. These solutions were then titrated with silver nitrate (approximately $N/14$), phenosafranine being used as indicator. The solution which had been diluted with water gave very sharp end-points, whereas that which contained nitric acid gave an incipient end-point when less than one-third of the volume of silver nitrate was run in from the burette. When shaken, however, the precipitate changed from blue to pink, and on addition of more silver nitrate, the same volume was ultimately required as in the former case. While valueless from the standpoint of quantitative accuracy, these experiments do give some qualitative verification of the action of hydrogen ions in restraining the transformation of the green univalent $[Cr(H_2O)_4Cl_2]^+$ ion into the violet tervalent $[Cr(H_2O)_6]^{+++}$ ion.

2. Weak Electrolytes.—That silver chloride is soluble in mercuric nitrate solution was known to Wackenroder, and recognised by Stas as a source of error in the determination of silver in presence of mercuric salts. It was not surprising, therefore, to find that titrations of mercuric chloride by means of silver nitrate with adsorption indicators should be unsuccessful. More unexpected, however, were the highly irregular results which were obtained when thallic halides were titrated in this way with silver nitrate. The thallic halides resemble the mercuric halides to some extent in being weak electrolytes (Berry and Lowry, *J. Chem. Soc.*, 1928, 1748), and also in having a marked tendency to form complex ions. It is particularly to be noted that this is a property of thall*ic* ions, and does not in any way apply to thall*ous* ions. It was found that the end-points with adsorption indicators in titrations with hydrochloric acid and silver nitrate were in no way altered in the presence of considerable quantities of thallous nitrate, in whichever way the titrations were carried out. The disturbing action of thallic ions was demonstrated by numerous experiments, of which the following may be described as the most impressive.

Equal volumes of a solution of silver nitrate (approximately $N/14$) were diluted, in one experiment with an equal volume of N nitric acid, and in the other with an equal volume of the same acid containing a small quantity of thallic oxide in solution. These solutions were titrated with $N/20$ hydrochloric acid.

When the silver nitrate solutions were titrated with the hydrochloric acid run in from the burette, with tartrazine as indicator, the quantity of acid required was approximately 20 per cent. *greater* in the solution containing the thallic salt. If the titration was carried out in the reverse direction, with phenosafranine as indicator, the volume of the silver solution required was approximately 21 per cent. *less* in the solution which contained the thallic nitrate than in the other. Moreover, the end-points were indistinct in all the titrations in which thallic nitrate was present. These differences were considerably accentuated when potassium bromide was used instead of hydrochloric acid for the titrations. Further confirmation of these irregularities was obtained in numerous analyses of thallium sesquichloride, $TlCl_3.3TlCl$, a salt which is easy to prepare in a high degree of purity. One further observation on this subject may be quoted: thallic oxide is much more rapidly dissolved by $N/10$ hydrochloric acid than by N nitric acid, thereby showing the tendency of thallic ions to combine with chlorine ions.

In titrations involving the use of adsorption indicators, it is frequently desirable to aid flocculation of the silver halide. This may be easily effected by adding a small quantity of a bivalent electrolyte, such as strontium nitrate, or, better still, of a tervalent electrolyte, such as lanthanum nitrate.

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Notes

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

THE USE OF ULTRA-VIOLET LIGHT FOR THE DETECTION OF TRACES OF SULPHITES

AT the suggestion of Mr. J. A. Radley, we have made a series of experiments on the detection of sulphites by oxidation to sulphuric acid and formation of the fluorescent quinine sulphate.

A boiling-tube was fitted with a tap-funnel, and an outlet consisting of an inverted U-tube with a bulb blown in each leg. This delivered into a test-tube immersed in cold water and containing 5 c.c. of boiled distilled water and 1 c.c. (or less) of the purest hydrogen peroxide (40 vol.) obtainable. About 10 c.c. of a solution containing known amounts of potassium sulphite were measured into the boiling-tube, sufficient 50 per cent. hydrochloric acid to acidify the mixture was added through the tap-funnel, and the whole was boiled gently so as to distil over 2 or 3 c.c. of water. The contents of the test-tube were then shaken well with a speck of quinine and examined in filtered ultra-violet light, when the presence of 0·25 mgrm. or more of sulphur dioxide was indicated by the brilliant violet fluorescence of quinine sulphate.

The only disadvantage of the method is the great sensitiveness of the fluorescence reaction. In the first place, it is extremely difficult to obtain a sample of hydrogen peroxide or of bromine water which does not itself fluoresce with quinine, and, for this reason, the minimum quantity of the former must be used. Secondly, care must be taken that no spray reaches the test-tube during the distillation. Attempts to increase the sensitiveness by adding powdered calcium

carbonate to the acid solution, so as to produce a non-oxidising atmosphere of carbon dioxide, were not successful, as a fluorescence was obtained without addition of sulphite. When phosphoric acid was used in place of hydrochloric acid high blanks were again obtained, and it should be noted that quinine phosphate also fluoresces in filtered ultra-violet light. The blank fluorescence obtained under the experimental conditions recommended above is, however, too weak to be confused with that from 0·25 mgrm. of SO_2.

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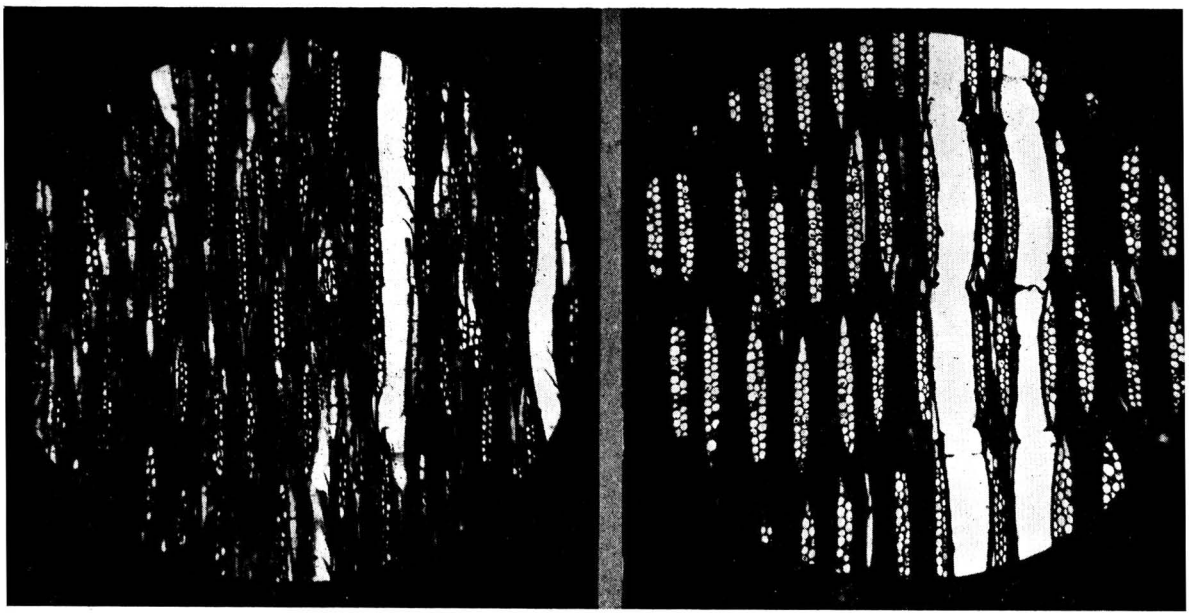
SANDALWOOD AND ITS SUBSTITUTES

THE two photomicrographs reproduced in the February issue of THE ANALYST (p. 124), representing tangential longitudinal sections of sandalwood and kalamet wood, respectively, do not show with sufficient clearness the structures intended.



Sandalwood (*Santalum album*) Kalamet Wood (*Mansonia Gagei*)

Tangential longitudinal Sections magnified × 50 lin.

The accompanying photomicrographs, taken at a higher magnification (×50), show the storage rays more clearly. It will be seen that the rays (*viz.* the lenticular, porous zones) of kalamet wood (*Mansonia Gagei*) are arranged in tiers, or stories, which appear to the naked eye or when examined with a hand-lens as "ripple marks." These form a feature of specific, diagnostic value in certain woods, and may be seen on polished longitudinal sections as fine parallel lines; the average number per inch is worth recording for any given species.

It should be noted that in true sandalwood (*Santalum album*), on the other hand, the rays possess no such definite arrangement.

In the last line of the original note, "Fig. 3" should read "Fig. 4."

3, RAWLINSON ROAD, OXFORD J. CECIL MABY

POISONING BY CARBON MONOXIDE FROM A GAS-HEATER

ON December 19th, 1931, a man and woman, aged 25 and 49, respectively, were seen about 5 a.m. by the man's brother, who slept in a room leading out of their room. He thought at that time that nothing was wrong, and it was not until 11 a.m. that, on passing through the room a second time, his suspicions were aroused, and he informed the police, and the man and woman, who were unconscious, were taken to a hospital. On both occasions when he passed through the room he had noticed that the man was lying in bed and that the woman was in a sitting position on the floor. The woman died after a known period of unconsciousness of about 24 hours. The man recovered after a period of unconsciousness of about 36 hours. The former was deeply unconscious all the time, but in the latter unconsciousness was light.

Clinically, except for slight cyanosis, dilated but reacting pupils, an irregular feeble pulse, and the fact that the man had vomited prior to admission, there was no evidence of poisoning, but the taking of a narcotic poison was presumed.

The post-mortem findings in the case of the woman were quite negative, as was also the analysis of the viscera. The blood of the woman contained no carbon monoxide. No poison was detected in the vomit of the man. A small bottle of tablets of two kinds (aspirin and potassium chlorate) was found in the room.

The man, on recovery, denied that there was a suicide pact, or that he had taken poison. He could not account in any way for what had happened, and remembered nothing after getting into bed. He was living, he said, happily, and was in regular work.

In view of the negative findings, an enquiry was made about coal-gas poisoning. The brother who had passed through the room had smelt nothing, and the police found the gas-taps in order, and the gas-meter was of a quarterly variety. When the police arrived, a small gas-stove was burning in the room; it was subsequently elicited that the occupants of the room were not in the habit of leaving the stove burning all night. At this time, some six weeks after the tragedy, I requested that the gas-stove should be sent to me. It had been sold, and, after some difficulty, was found by the police in a second-hand dealer's shop, and was sent to me. I further elicited the fact that it was not connected with the chimney in the room, and that the regulator of the chimney was closed, so that all fumes from the burning stove must have been discharged into the room. The gas-stove was of a very old-fashioned pattern, and one which might be expected to produce carbon monoxide.

The room occupied by these persons was 13 ft. 3 in. by 11 ft. 4 in. by 8 ft. It had two doors, one of which was closed and the other open to the width of a crack, and one window, which was closed, except for a quarter of an inch at the top. The bed was between the stove and the door leading to the second room, which was also the one open the width of a crack. The man was found lying on the side of the bed nearer to the slightly open door, and the woman was found on the floor on the opposite side of the bed, *i.e.* away from the slightly open door.

I arranged for the stove to be sent to the Government Chemist, and his report, based on work done by Mr. L. C. Nickolls, of that department, is most interesting, and is here given in detail.

REPORT OF THE GOVERNMENT CHEMIST.—"The gas-heater has been tested under varying conditions of gas consumption and air supply.

"When the heater is burning its maximum quantity of from 10 to 12 cubic feet of gas per hour, the amount of carbon monoxide in the products of combustion is approximately 2 parts in 10,000, equivalent to 20 parts in 10,000 of the gas

burned, and the equilibrium concentration in the air of the room (13 ft. 3 in. × 11 ft. 4 in. × 8 ft. = 1200 cb. ft.) is:

Assuming:	½ air-change per hour	1 air-change per hour	2 air-changes per hour
	0·5	0·25	0·1 part in 10,000

"These concentrations of carbon monoxide are innocuous. Similarly, when the gas supply to the heater is reduced to 5 cubic feet an hour, no increase in the quantity of carbon monoxide produced is observed. When, however, the gas supply is maintained at about 8 cubic feet per hour, a critical condition exists in the behaviour of the heater, and, irrespective of alterations in the air supply, relatively very large quantities of carbon monoxide are produced, and dangerous concentrations in the air of the room might be obtained.

"In one experiment the exit gases from the heater contained 71 parts in 10,000 of carbon monoxide (equivalent to 1780 parts in 10,000 of the gas burned), and the equilibrium concentration in the above room would be:

Assuming:	½ air-change per hour	1 air-change per hour	2 air-changes per hour
	24	12	6 parts in 10,000

"The two former concentrations are lethal, the last after some hours' exposure might prove lethal.

"The probable number of air changes an hour in the room in question is based upon the following considerations:—In the first report of the Departmental Committee to enquire into the ventilation of factories and workshops, 1902 (Appendix II, p. 105), it is stated that in small rooms having all apertures closed the ventilation varies from ⅓ to 2 air-changes an hour, while the Director of the Building Research Station, Department of Scientific and Industrial Research, has reported that the air-changes in a closed room may vary from ½ to 1½ an hour."

Effect of Carbon Monoxide.—If about one-half of the blood is unavailable for carrying oxygen (*i.e.* 50 per cent. saturation with carbon monoxide), the patient will be seriously ill, but, if removed from the vitiated atmosphere, will recover in many instances. If, however, such a saturation is maintained in his blood for a period of hours, it follows that during this time sufficient oxygen is not reaching the body, particularly the brain, with the result that the latter becomes damaged. Although the patient when removed from the vitiated atmosphere rids himself of the carbon monoxide, the damage which has already taken place to the brain-cells is such that unconsciousness persists, and the patient may die. This distinction is important, as the person who puts his head in a gas-oven, for example, and dies in a few minutes, dies directly from the effects of poisoning by carbon monoxide.

Evidence of Carbon Monoxide Poisoning on Arrival of the Patients at the Hospital.—According to the times given to me, about two hours elapsed between the calling of the police and the arrival at the hospital. As soon as patients are removed from the influence of carbon monoxide by ventilation of the room or by being taken into the open air, the concentration of carbon monoxide in the blood rapidly diminishes, and, no doubt, when the patients arrived at the hospital, there was no clinical evidence of poisoning. It is stated that carbon monoxide can disappear from the blood in 30 minutes in fresh air.

Long Period of Unconsciousness in Hospital.—In rapidly fatal cases of carbon monoxide poisoning, death is due directly to the gas. In the cases in question, saturation was slow and never reached a very high level, but exposure was of considerable length. Death was probably due to damage to the brain cells from this long exposure. In the case of the man the damage was less serious, so recovery ensued.

Recovery of the Man and Death of the Woman.—The position of the man in bed, that is to say, nearer the slightly open door, suggests that some ventilation in the form of incoming currents of air resulted in his receiving a lower concentration of carbon monoxide in the air that he breathed, so that the percentage saturation in his blood was less. This is supported by the fact that when the police found him he was not fully unconscious. The position of the woman was very characteristic ("the woman, herself, being in a sitting position on the floor"). No doubt she realised at some time during the night that the stove was still burning, and attempted to get out of bed to extinguish it. When persons are partly under the influence of carbon monoxide, the slightest muscular effort, *e.g.* getting out of bed, is accompanied by great breathlessness, resulting in the inhaling of still more carbon monoxide, and great muscular weakness. As soon as she got out of bed, she immediately collapsed on the floor, and found herself unable to move. As she was well away from the window and the door, the concentration of carbon monoxide reached a higher level in her blood than in that of the man, so that, when found, she was fully unconscious, and during the time which elapsed between the gassing and the giving of the alarm, the percentage saturation in her blood was maintained at a sufficiently high level to produce ultimately a fatal result.

History of the Exposure.—Assuming that the stove was lit about midnight, and that the patients were first seen about 5 to 6 a.m., there had been from 5 to 6 hours' exposure. The brother then walked through the room and, no doubt, caused some temporary ventilation. The two persons were then exposed for another 5 hours. As the concentration in the room for the first few hours that the stove was burning would be very low, it may be assumed that they had about 7 hours of effective exposure to a noxious concentration of carbon monoxide in the air of the room.

When the blood is about 25 per cent. saturated with carbon monoxide, the first symptoms appear; at 30 to 35 per cent. definite symptoms, such as increased breathing, muscular weakness, giddiness, etc., occur; at 50 per cent. the symptoms become urgent; at 50 to 60 per cent. unconsciousness supervenes; and at 65 to 85 per cent. death will occur. In the case of the man, the highest percentage reached in the blood was probably about 50 per cent., and for the woman the percentage was rather higher. Breathing 15 to 20 parts of carbon monoxide in the air per 10,000 parts can cause death in 4 hours and upwards, that is to say, at 65 to 85 per cent. saturation. In these cases I suggested that about 50 per cent. saturation occurred, and that it was maintained for about 7 hours. Therefore, it is fair to assume that the concentration in the air of the room was, for most of the time, considerably less than 15 parts per 10,000 of carbon monoxide. From the report of the Government Chemist, it is evident that, even with 1 air-change per hour, the concentrations I postulated in the blood of these people could easily have been attained.

G. ROCHE LYNCH

DEPARTMENT OF CHEMICAL PATHOLOGY,
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LONDON, W.1

Official Appointments

THE Minister of Health has approved the appointment of:

JAMES THOMPSON, Ph.D., F.I.C., as Public Analyst for the County of Berkshire, in place of Sir W. R. Smith (deceased).

The appointment of ALAN WEST STEWART as Additional Analyst terminates on the appointment of James Thompson as successor to the late Sir W. R. Smith (June 15th, 1932).

ALAN WEST STEWART, D.Sc., F.I.C., as Public Analyst for the Metropolitan Borough of Paddington (June 22nd, 1932).

The Minister of Agriculture and Fisheries has confirmed the following appointments:

HAROLD LOWE, M.Sc., F.I.C., previously Deputy Agricultural Analyst, now appointed Agricultural Analyst for the County of Denbigh, vice W. F. Lowe (deceased).

J. AUGUSTUS VOELCKER, C.I.E., M.A., Ph.D., F.I.C., as Agricultural Analyst for the County Borough of Oxford, vice Sir W. R. Smith (deceased).

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.

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1932

OF the 1285 samples examined under the Food and Drugs Act during the quarter, 110 were formal and 1175 informal; 83 were adulterated or incorrect. Seventy-one of the 668 samples of milk were condemned.

LABELLING OF JAM.—Three informal samples of jam had the name of the jam on the label in very large type and the words "with other fruit juice" in very small type. The Food Manufacturers' Federation was informed of the conditions on which manufacturers are allowed to use the Federation label.

GREY POWDER TABLETS.—These were half-grain tablets and should have contained one-sixth of a grain of mercury and one-third of a grain of chalk in each tablet. In this sample the mercury was 20 per cent. deficient. The vendor was communicated with, and later a letter was received from the wholesale dealers supplying him, stating that the deficiency was probably due to the fact that the tablets had been in stock about four and a half years. Experiments made by them had established the fact that loss of mercury occurred if grey powder tablets were kept in stock for too long a period.

This explanation is quite reasonable, since mercury is volatile even at temperatures below freezing-point. The vendor was warned that grey powder tablets should not be kept in stock for a longer period than six months, in which time the loss of mercury would probably be less than 5 per cent.

H. H. BAGNALL

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.

"HONEY AND BUTTER ROCK" WITHOUT HONEY

On June 14th a Plymouth firm of wholesale sweet manufacturers was summoned at Camborne, Cornwall, for selling at Redruth, on February 13th, honey and butter rock bearing a false label. Originally the Cornwall County Council had proceeded against a firm of grocers, and when the case was dismissed after the production of a warranty, a summons had been issued against the wholesalers.

Mr. W. W. Johnston, for the County Council, said that the jar containing the sweets stated that they were guaranteed to be pure and to comply with the Food and Drugs Act. The Public Analyst (Dr. H. E. Cox) had certified that the rock consisted of cane sugar with a little butter, but contained no honey.

For the defence, it was contended that the rock had to be boiled at a high temperature, and that if a lot of butter and honey were put in, the sweets would lose their real properties. The defendants had realised all along that the label was misleading. There was no necessity for them to alter the sweets, but there would be a new label which would comply completely with the Act.

The Bench imposed a fine of £5.

Department of Scientific and Industrial Research

FOOD INVESTIGATION

THE YELLOWING OF THE ABDOMINAL FAT OF FROZEN RABBITS*

If the fatty tissues of the wild rabbit (*Lepus cuniculus*) are stored at temperatures below the freezing-point of water, the exposed surfaces frequently acquire a pronounced yellow colour, which may even deepen to orange, and is accompanied by a sharp odour resembling that of "blown" linseed oil. An apparently similar type of yellowing occurs on certain slowly frozen fish. The period between the killing of rabbits in Australia and marketing in this country varies considerably, probably averaging 4 to 5 months. The temperature at which they are held during the voyage probably averages about −10° C. Experiments, having in view a study of the pre-freezing treatment, and temperature and duration of storage, were carried out in England on trapped rabbits. The fat is semi-liquid at body temperature, and is still soft at −10° C.; and films exposed to the air set slowly with moderately tenacious skins. The fat is highly unsaturated, the iodine values for those used in this work varying from 119 to 179. To determine the degree of yellowing, the yellow fraction was separated from the total fatty acids. The dissected yellow fat was ground with sand, dried over anhydrous

* Special Report No. 42, by J. R. Vickery. Obtainable at Adastral House, Kingsway, W.C.2. Price 6d. net.

sodium sulphate, treated with alcohol until no further colour was extracted, the alcohol was evaporated, and 2 to 3 grms. of the fatty acids were treated with 100 c.c. of petroleum spirit. The yellow fraction was precipitated on the walls of the vessel, and cooling for several hours at about +5° C. was necessary to complete separation. The precipitated fraction was washed with petroleum spirit, most of the solvent was removed, and the fraction was dissolved in hot absolute alcohol. This was removed and the fraction was weighed. Attempts to estimate the degree of yellowing were also made, but colorimetric comparisons of the fats were not practicable, owing to the insolubility of the deeply-coloured fats in all solvents but hot alcohol. Statistical comparisons, however, were made by examination at definite intervals. The storage experiments showed that yellowness could be produced in the fat by storing the rabbits for a sufficient time in the frozen condition, the yellowness becoming more pronounced as storage proceeded; the standards of colour adopted were pale yellow, dark yellow, orange, and dark orange. The difficulty of allowing for the varying amounts of adipose tissue was found not to be serious. After the initial latent period, intensity and depth of penetration of the yellowness were found to be approximately proportional to the duration of storage at a given temperature, being greater the higher the temperature. The duration and temperature of storage in the pre-freezing period are responsible for the rapidity of yellowing, storage for two days at atmospheric temperature subsequently enhancing yellowing to approximately the same degree as one month's storage at −5° C. At −18° C., yellowing is, commercially, almost prevented, and the duration of storage sufficient to affect the market value of rabbits kept at −10·5° C., varied from 3 to 5 months according to the pre-freezing treatment used. The investigation of the causes of yellowing included a study of the effect of micro-organisms, but these were definitely excluded as a cause of the phenomenon. The evidence for this particular type of oxidation by atmospheric oxygen as the cause of pigmentation is largely circumstantial, but the possibility of the liberation of an enzyme which catalyses the yellowing process in the fat cells during freezing is regarded as possible. Further, the presence of water and blood (haemoglobin) was found to exert a marked accelerating influence on the process. The yellow fraction is regarded as originating in the oxidation of the linoleate glycerides in the presence of an oxidase with or without water and haemoglobin in the fatty tissues, and the pigment itself is probably an unsaturated ketonic compound. It may be that the rate of yellowing in fats stored at a fixed temperature is greater the lower their initial iodine values. The necessity for storing the carcases in the frozen condition for as short a period as possible, in both the exporting and importing countries, is emphasised, and, so far as is possible, the temperature of storage should be not higher than −14° C.

D. G. H.

International Vitamin Standards

In June of last year, under the auspices of the Permanent Commission on Biological Standardisation of the Health Organisation of the League of Nations, a Conference of experts was held in London with the object of discussing the possibility of adopting standards and defining units for certain of the vitamins. As a result of their deliberations the Conference made a series of important recommendations to the Permanent Standards Commission, and these are set out in the Report [No. C.H. 1055 (1)],* Briefly, the Conference recommended the adoption of a standard, and the definition of a unit in terms of such standard, for the four vitamins *A*, B_1, *C* and *D*. The Conference further recommended that in the case of the two vitamins, *A* and *D*, the final preparation of the standard should be undertaken by the National Institute for Medical Research, Hampstead, and that the standard for vitamin B_1 should be prepared in Java. The

* Obtainable from Messrs. Allen & Unwin, 40 Museum Street, W.C.1

National Institute at Hampstead was further nominated to act, on behalf of the Health Organisation of the League of Nations, as the central laboratory for the storage and distribution of the three standard preparations for vitamins *A*, B_1 and *D*. In the case of vitamins *A*, *C* and *D*, it was recommended that the proposed standards and units should be adopted for a period of two years in the first instance, the standard for vitamin B_1 being given a preliminary currency of five years. In the case of vitamin *C* no preparation or storage of a stable standard was involved by the recommendation of the Conference which was satisfied, for this vitamin, to recommend the use of fresh lemon juice as a standard, and to define the unit as the anti-scorbutic activity of 0·1 c.c. of the juice, prepared according to a simple method described in the Report.

VITAMIN *A*.—Carotene was recommended as the international standard for vitamin *A*, and the unit was defined as the vitamin *A* activity of 1γ (0·001 mgrm.) of the standard preparation of carotene. Eight laboratories have contributed varying quantities of carotene, and these have been mixed at the National Institute for Medical Research; the mixed carotene has been purified by recrystallisation until the melting point is above 179° C. The highly purified preparation has been distributed in 10-mgrm. quantities into small ampoules in an atmosphere of pure nitrogen, reduced to dryness, and the ampoules sealed.

VITAMIN *D*.—With regard to the international standard for vitamin *D*, the Conference recommended that the standard solution of irradiated ergosterol, which has been issued from the National Institute for Medical Research, Hampstead, for the past two years (*cf.* ANALYST, 1930, **55**, 692; 1932, 174), should be adopted as the international standard. On account of the fact that this standard preparation had been intended, primarily, for the needs of this country alone, it was considered desirable to prepare a larger quantity to meet the needs of other interested countries—19 in all—for a period of some years. Accordingly, a second and larger quantity of irradiated ergosterol has been prepared at the National Institute for Medical Research, and this has been assayed in terms of the original standard preparation. The comparative examination of the new and the original standard preparations has been carried out by eight different laboratories in five different countries, and these eight groups of workers are unanimous in agreeing that the new standard now available is exactly equivalent to the original standard. There is, accordingly, now available an adequate amount of this standard preparation of vitamin *D* to meet the requirements of all workers throughout the world for some years to come. The unit recommended for international use is defined as the vitamin *D* activity of 1 mgrm. of the international standard solution of irradiated ergosterol.

VITAMIN B_1.—The standard for vitamin B_1 recommended for international adoption is a concentrated preparation of the anti-neuritic vitamin B_1, adsorbed on kaolin. The standard has been prepared in the Medical Laboratory, Batavia, Java, and is stored at the National Institute for Medical Research, Hampstead, from which it will be distributed. The international unit has been defined as the anti-neuritic activity of 10 mgrms. of the international standard preparation. The standard preparation is very stable, and, provided it is protected from moisture, appears to retain its activity unchanged.

In the case of other countries, arrangements have been made to send suitable supplies of each of the above standards to approved national institutions for local distribution. Institutions or individual investigators in Great Britain and Ireland, who wish to obtain supplies of one or more of these standards, should apply to the Department of Biological Standards, National Institute for Medical Research, N.W.3, from which issues will be made at regular intervals.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Composition of Shell Eggs. L. C. Mitchell. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 310–326.)—The methods used for determining total solids, chlorine, phosphorus, organic and ammoniacal nitrogen, and dextrose, are those described in *Methods of Analysis* (*A.O.A.C.*), 1930, 244–249. Crude albumin nitrogen is taken to be the water-soluble nitrogen precipitable by 40 per cent. alcohol. The fat was determined by hydrolysis as follows:—Approximately 2 grms. of yolks, or 3 grms. of whole eggs, or 5 grms. of whites, are weighed accurately by difference from the well-mixed sample into a Mojonnier fat-extraction tube, 10 c.c. of

concentrated hydrochloric acid being then added slowly and with vigorous shaking. The tube is placed in a water-bath at 70° C., this being then brought to the boiling point and kept boiling for 30 minutes, during which time the tube is carefully shaken at five-minute intervals. The tube is afterwards removed from the bath, and, after addition of water (better than alcohol) to fill the lower bulb of the tube, cooled to room temperature. The contents of the tube are next mixed, first with 25 c.c. of ether and then with 25 c.c. of redistilled petroleum spirit (b.pt. below 60° C.), and allowed to stand until the ethereal layer becomes clear. This layer is decanted into a weighed 125-c.c. beaker-flask containing two or three porcelain chips, the solvent being evaporated slowly on a water-bath. The residual liquid is subjected to two further extractions, 15 c.c. of each of the two solvents being used each time and mixed in separately as before. The clear solvent layer is again decanted into the beaker-flask, and the residue left on evaporation of the solvent is dried at 100° C. to minimum weight. The vessel is then left in the air until it no longer changes in weight. The weight of the residue thus obtained is corrected by a blank determination on the reagents.

Numerous data, referring to two-day-old eggs, commercial fresh eggs, and storage eggs separately, are given. The outstanding feature of the results is the uniformity in composition shown by fresh eggs. Certain changes in composition with increasing age of the egg are indicated, and further work in this direction will be reported later. Both whites and yolks separated from fresh and storage eggs exhibit differences in composition which indicate osmotic action, and suggest a possible means of ascertaining the freshness of eggs. T. H. P.

Decomposition of Lecithin in Eggs. L. C. Mitchell. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 282–284.)—A sample of whole eggs, broken under presumably aseptic conditions just before being sent by post to various analysts, gave percentages of lipoid phosphorus (as P_2O_5), varying from 0·37 to 0·08. The control sample was divided into a number of portions, which were analysed from time to time until they became putrid. With some of these portions, which exhibited normal putridity, the proportion of lipoid and of phosphoric anhydride in the lipoid suffered little change. With others, which developed a creamy colour and a pasty consistence, the percentage of lipoid diminished slightly, and that of phosphoric anhydride in the lipoid enormously; the nitrogen also decreased markedly, and the acidity showed a large increase. For the lipoids of two of the portions the following results were obtained:

	Lipoid present Per Cent.	Phosphoric anhydride Per Cent.	Nitrogen Per Cent.	Acidity in c.c. of C_2H_5ONa per grm.
Putridity normal	12·68	2·67	0·55	4·0
Putridity abnormal	11·54	0·17	0·16	60·0

The decomposition of lipoid material occurring in the abnormal cases evidently involves a breakdown of the lecithin, with formation of fatty acid and disappearance of lipoid phosphorus and choline nitrogen. That this change is due to bacterial growth is shown by the observation that inoculation of fresh eggs with the abnormal eggs induces similar changes. The bacteria apparently produce the enzyme lecithinase, which attacks lecithin. T. H. P.

Determination of Nitrogen in Yeast by the Hydrogenation Method. H. ter Meulen and K. Peeren. (*J. Inst. Brewing*, 1932, **38**, 330–331.)—As a result of the erratic results obtained by Thorne (*id.*, 1932, **38**, 28), further details of ter Meulen's method (*Rec. Trav. Chim. Pays-Bas*, 1924, **43**, 643; 1930, **49**, 396) are given. One c.c. of a 1 per cent. suspension of the sample in water is mixed with 0·5 grm. of nickel formate in a porcelain boat, and the mixture is then dried and heated in a current of hydrogen at 250° C., the gases being passed through 10 grms. of soda-lime (to trap any unchanged formic acid) and nickel-asbestos. The resulting ammonia is titrated with 0·01 *N* acid from a burette reading to 0·001 c.c. The determination takes 30 minutes, and the values for 10 samples of brewer's or baker's yeast, which were accurate to within about 0·002 mgrm., confirm the previous results, namely, that the method gives results from 0·8 to 19·1 per cent. higher than those obtained by the Kjeldahl–Gunning method, these differences being, on the whole, greater than those between the Gunning and Christensen–Fulmer modifications.

ABSTRACTOR'S NOTE.—It has been found that the most suitable apparatus for this method is a resistance-glass tube about 40 cm. long and 2 cm. in diameter, passed through holes in the ends of an asbestos or tin box 25 cm. long. The portion of the tube inside the box is packed with a catalyst consisting of an intimate mixture of asbestos and reduced nickel prepared by heating black nickel oxide in hydrogen at 320° C. Soda-lime is also required if halogens or sulphur are present. Nickel formate is prepared by the action of formic acid on precipitated nickel carbonate, and if 0·1 grm. is mixed with 0·05 grm. of sample and 0·5 grm. of reduced nickel, reduction is greatly facilitated. A blank determination should first be made to ensure that the apparatus is free from nitrogen, and the boat containing the sample is then inserted in the portion of the tube outside the box and heated in a current of hydrogen, gently at first, and, finally, to a red heat, the portion of the tube inside the box being maintained at 250 to 300° C. (inside temperature). J. G.

Volumetric Method for the Determination of Formic Acid in Fruit Juices and Fruit Syrups. G. v. Szelényi. (*Z. Unters. Lebensm.*, 1932, **63**, 534–541.)—In Fincke's method (*id.*, 1911, **21**, 1; **22**, 88; ANALYST, 1911, **36**, 103, 496) such quantity of reaction mixture should be chosen that at least 0·01 per cent. of mercuric chloride (added in the form of a solution containing 100 grms. of mercuric chloride and 30 grms. of sodium chloride per litre) is present. Preferable methods are as follows:—(1) The sample is subjected to preliminary treatment, as in Fincke's method, and a portion of the filtered distillate, corresponding with 10 to 30 c.c. of juice or 30 grms. of syrup, is mixed in a stoppered flask with 5 c.c. of a 10 per cent. solution of sodium acetate and 15 to 20 c.c. (x c.c.) of 0·1 *N* bromoacetic acid, the extent of the decolorisation being an indication of the amount of formic acid present ($HCOOH + Br_2 = CO_2 + 2HBr$). After 30 minutes 5 c.c. of a 10 per cent. solution of potassium iodide are added, and the mixture is titrated with 0·1 *N* sodium thiosulphate solution (y c.c.). Then $2{\cdot}3(x - y)$ gives the formic acid in mgrms. (allowance being made for any blank), with an error of 0·05 to 0·5 mgrm., whilst Fincke's method gives lower results. Blank tests with

samples of raspberry juice and syrup free from formic acid yielded 0·5 per cent. (on 10 c.c.) and 1 to 1·5 per cent. (on 30 grms.), respectively, the corresponding figures obtained by Fincke's method being appreciably higher. (2) Calcium formate is produced by the addition of calcium carbonate (*cf.* Fincke, *loc. cit.*), and 200 to 300 c.c. of the mixture are heated with 10 c.c. of 10 per cent. sodium carbonate solution, 20 c.c. of 0·1 *N* potassium permanganate solution being then added rapidly, followed, after 1 minute, by 1 or 2 c.c. of a 10 per cent. solution of zinc sulphate. This removes any colloidal manganese compounds and sharpens the end-point of the final titration, which is carried out with 0·1 *N* arsenic acid. Then 1 c.c. of 0·1 *N* potassium permanganate solution ≡ 2·3 mgrms. of formic acid (*cf.* Hanak and Kürschner, ANALYST, 1931, **56**, 116) is added. If 45 minutes are allowed for the oxidation stage, the procedure may be carried out in the cold, and the results, though slightly higher, have an error of only 0·02 to 0·3 mgrm., and, again, are more accurate than those obtained by Fincke's method. Method (2) is better for fruit juices than for syrups, as the latter give higher blanks and develop a yellow colour due to decomposition products of the sugars. J. G.

Aluminium in the Ash of Plant Materials, Fruit Juices, and Similar Products. L. Hart. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 285–289.)—With the accepted methods based on the initial precipitation of iron and aluminium as phosphates, if the aluminium is calculated by difference after the iron and phosphoric acid have been determined, the result is subject to the errors of such determinations, whilst the colorimetric method with aluminon (ammonium aurin-tricarboxylate) requires very small amounts (less than 0·1 mgrm.) of aluminium in the comparison solutions. In the method now proposed, aluminium and iron are separated at *p*H 4 as phosphates, which are then dissolved in acid; the iron is removed by means of cupferron, and the aluminium is precipitated with 8-hydroxyquinoline. The method has been developed primarily to determine aluminium in apple vinegar, and gives good results with a synthetic mixture having the composition of apple ash.

The reagents used are: (*a*) 0·04 per cent. solution of bromocresol green in alcohol; (*b*) 5 per cent. ammonium nitrate solution adjusted to *p*H 4 with acetic acid [yellow-green with (*a*)]; (*c*) 6 per cent. aqueous cupferron solution; (*d*) 2·5 per cent. 8-hydroxyquinoline solution, prepared by triturating 2·5 grms. of the reagent and 5 c.c. of glacial acetic acid, pouring into water at 60° C., cooling, filtering, and diluting to 100 c.c.; (*e*) aluminium-free ammonia, prepared by distilling ammonia solution into water until the resulting solution is at least of 20 *N* concentration; to be kept in a bottle lined with paraffin wax or ceresin; (*f*) 5 per cent. ammonia solution. A quantity of the substance containing 2 to 10 mgrms. of aluminium is ashed at a red heat in an electric muffle until carbon-free, the ash being moistened, dried and again heated, if necessary. The ash is dissolved in dilute hydrochloric acid (1 + 4), and any iron is oxidised with a few drops of nitric acid. Any residue is filtered off, ignited, fused with sodium and potassium carbonates, and dissolved in a little hydrochloric acid (1 + 4), the solution being added to the filtrate. Unless a fivefold excess of P_2O_5 over the equivalent of iron and aluminium is assured, 0·1 grm. of monopotassium phosphate is added. After addition of 1 to 2 c.c. of (*a*) and 10 c.c. of ammonium acetate solution the liquid is partly

neutralised with redistilled ammonia, and treated gradually, while gently boiling, with ammonium acetate solution until it assumes a yellow-green colour. It is boiled gently for 1 to 2 minutes to coagulate the precipitate, which is allowed to settle, filtered off on a 7 cm. Whatman No. 41 filter paper, washed two or three times with the cold ammonium nitrate solution, and transferred to the original beaker. The filter is washed into the beaker with hydrochloric acid, and then with hot water, the ferric and aluminium phosphates being dissolved, by heating if necessary. A few crystals of potassium monophosphate are added and re-precipitation at *p*H 4, as above, is effected. The precipitate is filtered off, washed two or three times with cold ammonium nitrate solution and transferred to a 150-c.c. Pyrex beaker, the residue being dissolved in a known quantity (not over 50 c.c.) of sulphuric acid (1 + 4). The percentage of sulphuric acid in the whole liquid (not above 100 c.c.) is adjusted to 10 to 12, the solution being treated at 10° C., and with gentle stirring, with a slight excess of fresh cupferron solution—formation of a white precipitate, which immediately redissolves, indicates excess. After settling for 2 or 3 minutes, the precipitate is collected, by means of gentle suction, on filter-paper supported by a platinum cone or in a Gooch crucible; the filtrate is caught in a 250-c.c. Pyrex beaker containing cupferron solution to indicate if precipitation is complete, and the precipitate is washed with cold 10 per cent. sulphuric acid containing 1·5 grm. of cupferron per litre. The filtrate is concentrated to about 50 c.c. on the steam-bath, and then evaporated with 10 c.c. of concentrated nitric acid until dense fumes appear. If the solution is not colourless it must be heated with a little more of the acid. The cold liquid is diluted to about 60 c.c. and filtered to remove silica, the filtrate being treated with a slight excess of 8-hydroxyquinoline (1 c.c. of the 2·5 per cent. solution ≡ 1·54 mgrm. of Al), and then with redistilled ammonia until precipitation occurs, a 5 c.c. excess of the ammonia being added. The liquid is digested at 60° to 70° C., until the precipitate coagulates, cooled in ice-water, and filtered through a tared Gooch crucible. The aluminium quinolate precipitate is washed with 5 per cent. ammonia containing a few drops of 8-hydroxyquinoline solution, and dried, at 110° C., to constant weight; it contains 5·87 per cent. of aluminium or 11·10 per cent. of aluminium oxide. A blank experiment on the reagents, together with about 0·01 grm. of iron as ferric salt, should not give more than 0·2 or 0·3 mgrm. of aluminium. If the iron is to be determined, the cupferron precipitate is washed with 10 per cent. ammonia solution, which converts it into ferric hydroxide. If a cloudiness is produced, a second filtration becomes necessary. T. H. P.

Determination of Starch in Feeding Stuffs. G. S. Fraps. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 304–307.)—The use of taka-diastase in the determination of starch in feeding stuffs is preferable to that of malt, as the correction for the sugars dissolved is smaller. By the official method of acid hydrolysis large amounts of pentosans are included, but the use of weaker acid (0·02 *N*) reduces the quantity of pentosans dissolved, and thereby increases the accuracy of the method. Correction may be made for the pentosans either by determining these or by applying a factor, the value of which is dependent on the nature of the material analysed. Since 1 part of dextrose corresponds with 0·9 part of starch,

and 1 part of pentose with 0·8799 part of pentosan, sufficiently exact results are obtained by subtracting the percentage of pentosan from that found for starch. As the proportions of the various pentose sugars produced by the hydrolysis of the pentosans are not known, the exact figures to be used for the reducing factors for copper and for conversion to pentosans are also unknown, but errors thus introduced are small if the percentage of pentosans dissolved by the acid is small. When the results are corrected, hydrolysis with 0·02 *N* acid gives approximately the same results for starch as that with either malt-diastase or taka-diastase.

The procedure recommended is as follows: 2·25 grms. of the material are extracted on a hardened filter paper with five successive 10-c.c. portions of ether, and are then washed, first with 150 c.c. of 10 per cent. alcohol solution, and afterwards with a little strong alcohol, and allowed to become nearly dry. The residue is transferred, with exactly 200 c.c. of water, to a crude fibre beaker. The mixture is heated to boiling point, treated with 20 c.c. of 0·2 *N* hydrochloric acid, boiled for 30 minutes, and filtered through asbestos into a flask; the residue is washed two or three times with hot water into the same flask, the total volume of liquid obtained being 300 c.c. The solution, mixed with 30 c.c. of hydrochloric acid (sp.gr. 1·125), is heated for 2½ hours in a boiling water-bath, cooled, and made up to 500 c.c. On 20 or 40 c.c., neutralised with sodium carbonate, the sugars are determined by the Munson and Walker method. To determine the pentosans, 150 c.c. of the 500 c.c. of solution are distilled with 65 c.c. (measured with a pipette) of concentrated hydrochloric acid in the usual way. T. H. P.

Fatty Acids Associated with Cassava Starch. L. Lehrman. (*J. Amer. Chem. Soc.*, **1932**, **54**, 2527–2530.)—Fat was removed from cassava starch by extraction with petroleum spirit, and the residue left on evaporation of the solvent was hydrolysed with hydrochloric acid. The resulting 0·1 per cent. of yellow semi-solid oil (iodine value 78·8) was removed by filtration, and the filtrate was tested for glycerol, with negative results. The unsaturated fatty acids were separated from the saturated fatty acids by the magnesium soap and alcohol method; the latter were identified by their neutralisation values, and the former by oxidation with an alkaline solution of potassium permanganate and extraction of the oxidation-products with chloroform, and then with hot water. Analysis of the resulting hydroxy-stearic acids showed that the original fatty acids contained palmitic, oleic and linolic acids. Bromination of a solution of the unsaturated fatty acids in cold anhydrous ether, and extraction of the resulting white precipitate (after being washed with cold ether and dried) with hot petroleum spirit, yielded hexabromostearic acid (m.pt. 80 to 81° C.), indicating the presence of linolenic acid; attempts to find hexahydroxystearic acid in the oxidation products (*vide supra*) were unsuccessful. The portion soluble in petroleum spirit was found to consist of tetrabromostearic acid, and this confirmed the presence of linolic acid, which was also indicated by the production of tetrahydroxystearic acid on oxidation. Tests for nitrogen, sulphur, phosphorus, halogens, and unsaponifiable matter in the fatty acids gave negative results.

J. G.

Determination of Reducing Sugars by Colorimetric Determination of Unreduced Copper. E. M. Emmert. (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 327–329.)—The method described results in considerable saving of time when compared with methods in which the cuprous oxide formed is separated quantitatively. The reagents required are as follows: (*a*) A solution containing 40 grms. of copper sulphate per litre; (*b*) a solution containing 200 grms. of Rochelle salt and 150 grms. of sodium hydroxide per litre; (*c*) a solution containing 0·25 grm. of pure dextrose per litre; (*d*) 20 per cent. (by vol.) ammonia solution.

To standardise the copper solution, 10 c.c. of (*c*), 5 c.c. of (*a*), and 5 c.c. of (*b*), in a 150 c.c.-Erlenmeyer flask, are heated to boiling on an asbestos gauze and boiled gently for exactly 3 minutes. The hot liquid is made up to 25 c.c. in a measuring flask, and then filtered as rapidly as possible through any ordinary filter paper able to retain the cuprous oxide, which is discarded. Exactly 5 c.c. of the filtrate are made up to 50 c.c. with reagent (*d*) in a measuring flask. The blue colour of this solution is compared with that produced by 5 c.c. of reagent (*a*) when subjected to the same procedure, except that the 10 c.c. of dextrose solution is replaced by 10 c.c. of water. The number of mgrms. (X) of dextrose equivalent to 5 c.c. of the copper sulphate solution is calculated from the formula: $X - XR/U = Y$, in which U is the colorimetric reading of reagent (*a*) without added dextrose, R the reading after reduction with dextrose, and Y the number of mgrms. of dextrose added. This standardisation should be made in duplicate or triplicate.

The approximate sugar content of the solution to be analysed is determined by boiling 10 c.c.-portions of it with different quantities of the mixture of copper sulphate and alkaline tartrate solutions. The sugar solution, if necessary, is diluted or evaporated until 10 c.c. contains from 5 to 20 mgrms. of reducing sugar, expressed as dextrose. Ten c.c. of the solution are then treated exactly as in the standardisation of the copper solution. If it is not possible to adjust the concentration of the sugar solution without destroying some of the reducing power, the amount of copper sulphate solution used may be lessened somewhat. When tested with 5 to 6 mgrms. of pure dextrose this method showed errors of +4 to +5 per cent.; with quantities ranging from 7 to 20 mgrms. of the sugar the errors varied from −3 to +3·3 per cent. T. H. P.

Determination of Reducing Sugars in Raw Sugars, etc., by the Pot Method. H. Main. (*Int. Sugar J.*, 1932, **34**, 213–217.)—For routine determination of reducing sugars, incremental titration with Fehling's solution in presence of methylene blue as internal indicator, as described by Lane and Eynon (ANALYST, 1923, **48**, 220, 277), gives satisfactory results, but the personal element may introduce inaccuracies. Moreover, the standard method of titration given by these authors involves factors difficult to standardise, namely, the time of heating to boiling and the rate of ebullition, and, in addition, any local heating of the concentrated alkaline solution may cause destruction of both sucrose and invert sugar. The volumetric method now described overcomes these and other objections, and yields extremely accurate results in the hands of operators with a minimum of experience.

It consists essentially in heating, in boiling water, three or more large test-tubes, containing Fehling's solution, methylene blue, and such different amounts of the sugar that, at the end of a definite time, some tubes are still blue, whilst one, at least, shows complete reduction of the cupric salt. The tubes used should be of nearly the same size and weight, those employed by the author being of Monax glass and having the length 150 mm., the internal diameter 38 mm., and the weight 50 to 55 grms. Floats inserted to prevent access of air to the solutions during the determination consist of similar tubes, making a sliding fit in the others and being conveniently drawn out to a taper about 100 mm. from the closed end to make a total length of 170 mm. The water-bath may be a 3-gallon oval iron kitchen pot, tinned inside and fitted with an overflow and with a sight-feed through which hot water is added continuously to replace loss by evaporation. The water must be kept boiling. While in the water-bath, the tubes are held in clips fitted to a frame.

Use is made of Soxhlet's modification of Fehling's solution, which contains: (1) 34·639 grms. of pure crystallised copper sulphate dissolved to 500 c.c.; (2) 173 grms. of Rochelle salt and 50 grms. of sodium hydroxide dissolved to 500 c.c. Equal volumes of (1) and (2) are mixed as required. The methylene blue indicator is a 1 per cent. aqueous solution. The standard invert sugar solution is prepared as described by Lane and Eynon (*loc. cit.*), and tested as follows:—Into three of the test-tubes are placed in order: 10 ml. of Fehling's solution (into each); 24·5, 25·0 and 25·5 ml., respectively, of the diluted sugar solution, prepared by neutralising 50 ml. of the standard invert sugar solution with caustic soda solution and diluting to 250 ml.; 2 drops of methylene blue indicator. The contents of each tube are mixed by gentle rotation, the floats being then inserted so that they rest on the liquid and entrap no air-bubbles. The tubes in the frame are placed in the boiling water and removed and inspected after exactly five minutes. If the middle tube shows complete reduction, and that with 24·5 ml. of sugar solution is still blue, 10 ml. of Fehling's solution are taken as equivalent to $24{\cdot}75 \times 0{\cdot}002$ grm. $=0{\cdot}0495$ grm. of invert sugar. Closer approximation may be attained by lessening the differences between the volumes of sugar solution in the different tubes. The mean between the volumes in the last blue and the first red tube is always taken as correct, except that, when the blue colour in any tube is seen to fade on removal from the bath, the actual volume in that tube is regarded as the true volume.

When sucrose is present together with invert sugar, the oxidising power of the Fehling's solution is apparently decreased, probably owing to partial inversion of the sucrose. Tables are, therefore, given for the volumes of Fehling's solution reduced by solutions of invert sugar containing various proportions of sucrose. When very small amounts of reducing sugars are to be determined, the action of the Fehling's solution is accelerated by mixing it with 5 N sodium hydroxide solution (1 vol. to 1 vol.). In this way the small percentages of invert sugar (0·01 to 0·001) in commercial white sugars may be determined accurately. The difficulty of judging the end-point in such cases, owing to the dichroism caused by the very fine state of division of the cuprous oxide, may be overcome by adding to the mixture of sugar solution and Fehling's solution, before heating, potassium ferrocyanide in the proportion of 1 mol. per 4 mols. of copper sulphate present; the ferrocyanide

(14·647 grms. of $K_4FeCy_6.3H_2O$) may be incorporated in the 500 c.c. of Fehling's solution (2) containing the Rochelle salt and sodium hydroxide. This solution keeps unchanged for months. The procedure followed is that described above, except that for sugars containing less than 0·01 per cent. of invert sugar the time of heating in the boiling water-bath is increased to 10 minutes. This modification is particularly suitable for use at night-time. A table is given also for this method of working. T. H. P.

New Volumetric Method for the Determination of Reducing Sugars. E. Haddon. (*La Revue Agricole*, 1931, No. 59, 131 ; *International Sugar Journal*, 1932, **34**, 43.)—The determination is made on the ordinary clarified solution without de-leading. To about 100 c.c. of the solution to be examined, four drops of a 1 per cent. methylene blue solution are added, and the coloured solution is introduced into the burette. Two c.c. or 4 c.c. of a 10 per cent. solution of potassium ferrocyanide are added to 5 c.c. or 10 c.c. of Fehling's solution, and the solution is titrated by adding the coloured solution gradually without letting the boiling slacken. The end of the reaction is a *sudden* disappearance of the blue colour; it is very sharp, and the results are concordant. This method, which is a simplification of published methods, will probably be useful to sugar-house chemists, especially when determinations are to be made at night.

Quince Seed Oil. W. H. Dickhart. (*Amer. J. Pharm.*, 1932, **104**, 335–336.) —*Cydonium* (quince) seeds contain about 22 per cent. of mucilage, and, when dried, about 15 per cent. of a fixed oil, amygdalin, tannin, colouring matter, and 13 per cent. of ash. As obtained by extraction with petroleum spirit a specimen of the oil had the following characteristics:—Specific gravity at 15° C., 0·9251; n_D^{40}, 1·4696; saponification value, 187·7; iodine value (Wijs), 112·4; free fatty acids (as oleic), 6·49 per cent.; unsaponifiable matter, 9·35 per cent.; n_D^{40} of free fatty acids, 1·4639; and iodine value, 100·5; total fatty acids, 90·4 per cent. The Halphen and Villavecchia tests were negative, but the Bellier test showed a trace of arachidic acid. D. G. H.

Oil from the Nuts of *Calophyllum inophyllum* (Dilo Oil). K. W. R. Glasgow. (*J. Soc. Chem. Ind.*, 1932, **51**, 172–174T.)—*Calophyllum inophyllum*, a tree indigenous to Fiji, is closely related to the trees producing such oils as laurel nut, domba, and Alexandrian laurel oils; also to tacamahaca fat, and poon-seed oil, Calabar, Njamplung and pinnay oils. The dry nuts contain about 40 per cent. of kernels, yielding, on extraction, about 43·5 per cent. of an amber oil, and, on a large scale by discontinuous extraction with hot ether, about 58 per cent. of oil. The oil melts at 50° C., but, when once completely melted, takes a considerable time to set again; it is a non-drying oil. The sample examined had sp.gr. at 21° C., 0·929; $n_D^{60°}$, 1·4680; saponification value, 200·9; iodine value, 81·7; free fatty acids (oleic), 33·9 per cent.; unsaponifiable matter, 0·25 per cent.; optical rotation, −9·8°. Six hours' treatment with pure oxygen decreased the iodine value to 64, the acid value remaining unaltered. The liquid and solid acids of the free acid portion were separated and examined, and these acids showed no radical difference from the acids separated from the neutral oil. The whole oil

was saponified, and the liberated acids, when examined by the Twitchell method, yielded 9·7 per cent. of resin acids, only abietic acid being identified. The remaining fatty acids yielded 31 per cent. of solid, and 69 per cent. of liquid acids, and, after separation and redistillation, the 90·30 per cent. present were found to consist of palmitic, 14·1; stearic, 11·0; erucic, 3·0; oleic, 48·0; and linolic acid, 14·3 per cent. The unsaponifiable matter contained sitosterol. D. G. H.

Determination of Veronal and of Mercury Tannate. A. Ionescu-Matiu and A. Popesco. (*J. Pharm. Chim.*, 1932, **124**, 551–554.)—*Veronal*: Two to 4 c.c. of a saturated solution of veronal are treated with 5 c.c. of a mercuric sulphate solution made by dissolving 5 grms. of mercuric oxide in 20 c.c. of concentrated sulphuric acid and 93 c.c. of water. A white precipitate is formed on shaking, and, after centrifuging, the opalescent supernatant liquid is decanted, and the precipitate is washed with 3 portions of 3 to 4 c.c. of water, and, finally, dissolved in a hot mixture of sulphuric and nitric acids (strength not given), the solution on dilution to 100 c.c. remaining clear. After addition of a few drops of permanganate solution (to destroy the nitrous compounds), the mercury is precipitated with 12 drops of a 10 per cent. solution of sodium nitroprusside. By means of a microburette a 0·1 *N* solution of sodium chloride is added until the cloudiness has disappeared. One c.c. of 0·1 *N* sodium chloride solution is equivalent to 0·01393 of veronal. The amounts of veronal found by this method agreed very closely with the amounts taken.

Mercury Tannate.—The tannate (0·02 to 0·15 grm.) is treated with 10 c.c. of a hot mixture of sulphuric and nitric acids (strength not given), the clear solution is diluted to 100 c.c., a few drops of 2 per cent. potassium permanganate solution are added, followed by 20 drops of 10 per cent. sodium nitroprusside solution to precipitate the mercury. Titration with 0·1 *N* sodium chloride solution then follows, and the number of c.c., multiplied by the factor 0·01785, gives the amount of mercury tannate originally present. D. G. H.

Biochemical

Body Fats of the Pig. II. Some Aspects of the Formation of Animal Depôt Fats Suggested by the Composition of their Glycerides and Fatty Acids. A. Banks and T. P. Hilditch. (*Biochem. J.*, 1932, **26**, 298–308.)—The whole of the leaf fat and a complete longitudinal section of the back fat, about 20 cm. wide, from a sow, have been subjected to a detailed survey of the component glycerides in the perinephric fat and in the layers on either side of the central seam of connective tissue in the back fat. The diet of the animal for about 15 months prior to slaughter had consisted of a mixture of wheat middlings (6 to 12 parts), barley meal (2½ to 5 parts), and fish-meal (½ to 1 part), with about 1 part of either extracted soya bean meal, dried milk, or cheese. The shoulder end of the back fat was noticeably softer than the main central portion. The data for component fatty acids of the pig fats are summarised. The most notable feature is the tendency for the united molar percentage of stearic, oleic and linolic acids to be in the neighbourhood of 70 per cent. Whatever the degree of saturation of a depôt fat, its molar content of C_{18} acids is near 70 per cent. (rising to about

73 per cent. with very unsaturated fats, and falling to about 65 per cent. in the more saturated fats). The actual degree of saturation is controlled, almost wholly, by the relative amounts of stearic and oleic acids present in any given case. The relative amounts of linolic and oleic acids in any pig fat seem to depend merely upon (1) the amount of stearic acid formation which has occurred, coupled with (2) the amount of linolic acid present in the mixed fatty acids as a whole; the latter depends to a large extent on the diet, and increases, but within comparatively narrow limits, from the perinephric to the outer layers of the back fats. The occurrence of 1 to 2 per cent. of unsaturated acids of the C_{20} and C_{22} series in all the depôt fats of a pig fed on a diet including fish-meal is noteworthy. As in the case of vegetable oils, the characteristic acids of ingested animal fat appear in pig depôt fats, but the C_{20} and C_{22} acids are not stored so freely as oleic and linolic acids. The results, on the whole, corroborate the general trade experience that a fish-meal diet leads to the production of extremely soft fat; the softness is due both to general increase in unsaturated components and, especially, to unusually large proportions of linolic acid. The C_{20} and C_{22} acids are not present in sufficient quantity to add appreciably to the soft qualities of the fats, but might well, with the onset of slight rancidity, be responsible for development of a fish-like taint in the flavour. The composition of storage fats leads the authors to favour the view that a hydrogenation of glycerides rather than of free fatty acids is an essential link in the process of their formation, but where this change may take place cannot be suggested with any confidence. The authors believe that the characteristic constancy at about 70 mols. per cent. of total C_{18} acids in pig depôt fats is most closely maintained when the diet of the animal has contained only small proportions of fat, and, accordingly, this may point to fat synthesised in the animal primarily from carbohydrate as being the main seat of the suggested hydrogenation process; but this does not preclude the possibility that directly assimilated fat may also be affected. On the other hand, the evidence of Ellis and Zeller (*J. Biol. Chem.*, 1930, **89**, 185), that linolic acid in pig depôt fat is derived exclusively from assimilated vegetable linolic acid, may indicate that assimilated fat from the diet does not undergo hydrogenation to any material extent. The tendency observed, in the less saturated depôt fats of a pig, for the component fatty acids to include somewhat more than 70 mols. per cent. of C_{18} acids, and, conversely, for the C_{18} acid molar content to fall below this figure in the more saturated depôt fats from the same animal, would be explicable if specific mixtures of glycerides were selectively withdrawn from the blood at different sites of deposition. This would presuppose the presence in the blood of a common stock of glycerides in which the chemical processes had been completed, a possibility which is perhaps less remote than the alternative of hydrogenation to varying degrees in the adipose tissues themselves. P. H. P.

Colorimetric Determination of Phosphorus. E. J. King. (*Biochem. J.*, 1932, **26**, 292–297.)—Several methods which have been described during recent years for the colorimetric determination of phosphorus are discussed. A new procedure is now proposed in which sulphuric acid is replaced by perchloric acid, which is a much better oxidising agent for the destruction of the organic material

in total phosphorus determinations. The procedure is a combination of those of Martland and Robison (*Biochem. J.*, 1926, **20**, 847) and Fiske and Subbarow (*J. Biol. Chem.*, 1925, **66**, 375; ANALYST, 1926, **51**, 205), and is believed to have advantages over the methods previously described. The colour is developed at a high acidity, as recommended by Martland and Robison, which allows of considerable variation without any loss in the proportionality of colour produced; hence no allowance is necessary for the presence of moderate amounts of trichloroacetic acid in test solutions; the acid and molybdate are kept separate. The full complement of blue colour is obtained in about 5 minutes by the use of 1:2:4-amino-naphtholsulphonic acid as the reducing agent. This is the agent suggested by Fiske and Subbarow, but it is made up in a slightly different way, since it has been found impossible to keep the sulphonic acid in solution in the proportions of bisulphite and sulphite recommended. Tables show some results obtained when perchloric acid was used in the presence of several interfering substances, and total phosphorus determinations on the barium salts of several phosphoric acid esters by the perchloric acid method; barium perchlorate is soluble in water, and so the barium need not be removed before analyses are made. The solutions required are: (1) 72 per cent. or 60 per cent. perchloric acid (the strength commonly obtainable on the market). One c.c. of 72 per cent. or 1·2 c.c. of 60 per cent. perchloric acid contains almost the same "total acidity" as 1 c.c. of 30 per cent. (by volume) sulphuric acid; (2) 5 per cent. ammonium molybdate; (3) 0·2 per cent. amino-naphtholsulphonic acid; 0·5 grm. of the 1:2:4-acid, 30 grms. sodium bisulphite and 6 grms. crystalline sodium sulphite are dissolved by shaking with enough water to make 250 c.c., and the solution is filtered until clear. The solution should be freshly prepared every 2 weeks. (4) Standard phosphate. For the stock solution 2·1935 grms. of pure potassium dihydrogen phosphate are dissolved in 500 c.c. of water; this solution contains 1·0 mgrm. phosphorus per c.c. For the dilute standard solution 5 c.c. of the stock solution are diluted to 500 c.c. with water; this solution contains 0·1 mgrm. phosphorus per 10 c.c. Both solutions must be kept saturated with chloroform. To determine the inorganic phosphate an amount of the solution to be tested is measured into a 15 c.c.-volumetric flask, and water is added to about 10 c.c. One c.c. of 72 per cent., or 1·2 c.c. of 60 per cent. perchloric acid, 1 c.c. of molybdate and 0·5 c.c. of the sulphonic acid are added, and water to 15 c.c. An appropriate standard (5 or 10 c.c. of the dilute standard solution) is similarly prepared at the same time. The contents of the flasks are gently shaken between each addition, and, finally, mixed by inversion and shaking. The colours are read after 5 minutes in a Duboscq colorimeter. With trichloroacetic acid filtrates of blood, urine, and other solutions where there is no barium present, it is preferable to use a mixed solution of 5 per cent. ammonium molybdate in 15 per cent. (by volume) sulphuric acid. Five or 10 c.c. of protein-free blood-filtrate, or 0·2 or 0·5 c.c. of urine are treated with 2 c.c. of the molybdate-sulphuric acid mixture, 0·5 c.c. of the sulphonic acid and water to 15 c.c. For total phosphate the sample is measured into an acid-resistant glass boiling-tube of about 1×6 in., 1·2 c.c. of 60 per cent. perchloric acid are added, and the contents of the tube are heated with a micro-burner or on an electric heater. The contents become concentrated, turn brown, then become colourless as the acid fumes; the organic

matter is completely oxidised in a few minutes. If the amount of organic material is large, a few drops of nitric acid, or of 30 per cent. hydrogen peroxide may be needed, and thus a little longer heating. The cooled contents of the tube are washed with several portions of water into a 15 c.c.-volumetric flask. To compensate for the loss during heating 0·2 c.c. of perchloric acid is added. One c.c. of molybdate and 0·5 c.c. of the sulphonic acid are then added to the test solution, and at the same time a standard is prepared from an appropriate number of c.c. of the dilute standard solution, 1·2 c.c. of perchloric acid, 1 c.c. of molybdate, and 0·5 c.c. of the sulphonic acid. The solution under examination and the standard are diluted to the mark, mixed, and read after 5 minutes. P. H. P.

Interpretation of the Colour Match in the Antimony Trichloride Test for Vitamin *A*. R. S. Morgan. (*Biochem. J.*, 1932, **26**, 377–380.)—It is known that the vitamin *A* potencies of very potent oils and concentrates, compared with a medicinal oil as standard, are lower than would be expected from their blue values. It is also known that the blue value of a medicinal grade oil determined *via* the unsaponifiable fraction is higher than the blue value determined directly. These discrepancies are attributed to the influence of varying colour quality on the blue component of the colour match. It is shown that the blue reading in the Lovibond match of a copper sulphate solution varies widely as the quality of the light from the solution is varied by the interposition of red glasses. The variation obtained is similar to that given in the colour matches on a wide range of oils and concentrates. It is also shown that the value for "blue *minus* yellow" can be expected to remain constant, however the redness of the solution varies, and it is considered that the value "blue *minus* yellow" would be a better criterion of vitamin *A* than the blue value as usually read. Biological tests and the fact that the "blue *minus* yellow" value of an oil determined *via* the unsaponifiable fraction agrees with the value determined directly, support this conclusion. Coward, Dyer, Morton and Gaddum (*Biochem. J.*, 1931, **25**, 1102; ANALYST, 1931, **56**, 821) compared the vitamin *A* potencies of 11 cod-liver oils and 2 concentrates, as biologically determined, with (among other things) the blue value of the oil determined directly and indirectly *via* the unsaponifiable matter. The blue value determined *via* the unsaponifiable matter gave better agreement with the biological determination of vitamin *A* than did the blue value determined directly. The author has examined oil A and oil L in the series assayed by Coward *et al.*; the colour matches determined were:

Oil A. 0·2 c.c. of a 10 per cent. solution: 5·5 blue+0·4 yellow.
Blue value=11·0.
"Blue *minus* yellow" value=10·2.

Oil L. 0·2 c.c. of a 0·35 per cent. solution: 5·5 blue+2·5 yellow−0·8 neutral.
Blue value=314.
"Blue *minus* yellow" value=171.

The ratio of the blue values of these oils is oil L/oil A=28·5/1, and the ratio of the "blue *minus* yellow" values is 16·8/1. The ratio of their biological values is given by Coward *et al.* as 15·6/1. P. H. P.

Vitamin Studies V. Chemical Methods for the Determination of Vitamins. I. Bezssonoff's Reaction. F. V. v. Hahn and M. Wieben. (*Z. Unters. Lebensm.*, 1932, **63**, 481–495.)—The work dealing with Bezssonoff's chemical reaction for vitamin *C* (ANALYST, 1921, **46**, 411, 462; 1924, **49**, 594;

1925, **50**, 517), and the quantitative modification proposed by Glassmann and Posdeew (*id.*, 1929, **54**, 432) are described and discussed, and it is concluded that the method has not yet been completely evaluated. Comparative tests were, therefore, made on guinea-pigs fed on a basal diet containing only traces of vitamin *C* and consisting of hay-extract, condensed milk (1:10) autoclaved at 130° C., egg-yolk, and freshly pressed yeast autolysed at 40° C., 23 samples of various fruits, 52 of vegetables, 20 of orange juice and 18 of preserves being tested. Where the guinea-pig unit was below 10, the percentages of samples giving a negative, weak, medium and strong Bezssonoff reaction were 30, 40, 30 and 0, respectively, the corresponding figures being 20, 30, 40 and 10 for 10 to 25 units; 0, 25, 60 and 15 for 25 to 100 units; and 0, 0, 30 and 70 for over 100 units. For 1:10 dilutions of sample there were 81, 77, 55 and 27 per cent. of negative reactions, respectively, and no strong reactions. The correspondence between the sugar content and the colour produced in the reaction observed by Glassmann and Posdeew (*loc. cit.*) was not confirmed. It is concluded that the reaction gives a rough indication of relative vitamin *C* contents, but must be judged with caution, as there are striking exceptions. Thus, pineapples and tomatoes give a strong reaction, but a low figure in tests on animals, whilst for black currants and many preserves these positions are reversed. Good agreement was obtained for spinach, and particularly for orange juices. The effect of cooking on vegetables was to lower both values, except in the case of Brussels sprouts, with which the biological value was unchanged and Bezssonoff's reaction was increased. J. G.

Accumulation of Molybdenum in Aquatic Plants. H. ter Meulen. (*Rec. Trav. Chim. Pays-Bas*, 1932, **51**, 549–550.)—The fresh-water plant *Azolla*, together with the small alga, *Anabaena Azollae*, with which it grows in symbiosis in the small canals about Delft, contains 1·13 mgrm. of molybdenum per kilo of dry material, the canal water itself containing only 0·0009 mgrm. of the metal per litre. The molybdenum probably plays a part in the fixation of atmospheric nitrogen by the alga. T. H. P.

Bacteriological

Viability of *Coli* Bacteria in Beer. R. Koch. (*Woch. Brau.*, 1932, **49**, 110–112,116–120; *J. Inst. Brewing*, 1932, **38**, 335–336.)—Pale lager beer was inoculated with about 1,000 million *B. coli* or related bacteria (10 strains) per c.c., with the result that the number fell below 1 million per c.c. after 5 to 25 days (according to the strain) at room temperature. The rate of decrease was slower at 4 to 5° C., in accordance with the general rule that antiseptics are less potent at low temperatures, but it was greater for more acidic beers (*e.g.* dark lagers). All cultures with a *p*H value over 4·4 contained *B. coli* after 25 days in the warm or cold, but at *p*H 3·6 to 3·8 the bacteria died within 15 days at room temperature, though they were still detectable after 25 days at 5° C.; for *p*H 3·0 to 3·2 they died within 5 days at 20° C., or within 15 days at 4° C. It is concluded that the acidity is the chief antiseptic influence in beer, the alcohol and carbon dioxide being of less importance. The inoculations were always very much greater than could occur in brewing

practice, even if the beer-bottles were rinsed with water containing one *B. coli* per c.c. In addition, the highly dangerous organisms which are sometimes found with *B. coli* of faecal origin occur in much smaller numbers than *B. coli*, and are destroyed even more rapidly in beer. J. G.

Detection of the Incipient Decomposition of Meat. G. Brotzu. (*Z. Unters. Lebensm.*, 1932, **63**, 503–514.)—The various proposed methods are criticised and compared for a number of samples of fresh and frozen meats stored for various periods (*cf.* Ottolenghi, *id.*, **1913**, **26**, 728; Grünhut, *id.*, 1919, **37**, 304; Henriques and Gjaldbäk, *Z. physiol. Chem.*, 1911, **75**, 363; Tillmans, Strohecker and Schütze, ANALYST, 1922, **47**, 78; Tillmans, Hirsch and Kuhn, *id.*, 1927, **52**, 289, etc.). If the amino acids are determined by the method of Ottolenghi or of Sörensen on 100 grms. of sample dried at 70° C., then the presence of 300 to 350 mgrms. of amino acid-nitrogen (based on titration to the third stage of Sörensen's method, *i.e.* to a weak red colour) indicates incipient decomposition. The methods of Grünhut and of Van Slyke also give satisfactory results and similar amino acid-time curves, 500 to 600 mgrms. being taken as a suitable limit in the latter case. The limiting *p*H value, determined on the warm meat juices, is 6·3. The data show no real distinction between fresh and frozen meat, except that in the latter case the amino acids are slightly higher. J. G.

Selective Fermentation of Glucose and Fructose by Yeast. E. R. Dawson. (*Biochem. J.*, 1932, **26**, 531–535.)—The author summarises the results published in the last decade on the selective fermentation of glucose and fructose by yeast. Willstätter and Sobotka (*Z. physiol. Chem.*, 1922, **123**, 170) expressed their results in terms of a selectivity constant $K = \frac{\ln y_o - \ln y}{\ln z_o - \ln z}$, where y_o and z_o represent the initial concentrations of glucose and fructose, and y and z represent sugar concentrations after a fermentation period, t. K is, therefore, the ratio of the separate velocity constants calculated for unimolecular reactions. The idea is expressed that the explanation of the phenomena of selective fermentation is to be found in the relative rates of fermentation of solutions containing low concentrations of the separate hexoses. According to the theory of Michaelis and Menten (*Biochem. Z.*, 1913, **49**, 333) the relative rates of reaction of two substrates competing for the same enzyme can be expressed by the formula $\frac{V_1K_2}{V_2K_1} = \frac{\ln y_o - \ln y}{\ln z_o - \ln z}$, where K_1 and K_2 are the Michaelis constants (expressed in concentrations) of the two substrates, and V_1 and V_2 the maximum velocities for each substrate alone. Since the maximum rates of fermentation of glucose and fructose by brewer's yeast are equal, it is evident that the above equation is identical with that used by Willstätter and Sobotka to express selectivity. The selectivity constant thus represents the ratio of the affinities of the two sugars for the enzyme. The author then analyses data obtained by Hopkins (*Biochem. J.*, 1931, **25**, 245), applies the Michaelis equation, and shows that the phenomena of selective fermentation by living yeast can be satisfactorily explained by the Michaelis theory of enzyme affinity. Living yeast possesses the power of adapting itself to the medium in

which it is propagated, and this type of adaptation must be considered as being due to an alteration in the affinity of the enzyme for the proffered substrate. The hypothesis is advanced that the selectivity shown by zymin when fermenting mixtures of glucose and fructose is controlled by the phosphate concentration. The author states that his treatment is no more than an outline of the methods by which it may be possible to arrive at an understanding of the factors which govern selective fermentation. P. H. P.

Toxicological

Distribution and Elimination of Bismuth in the Body. Paget, Langeron and Devriendt. (*J. Pharm. Chim.*, 1932, **124**, 600–608.)—Bismuth is found in the urine and faeces within 24 hours of injection, and elimination may last over a long period; for example, the period of elimination of 8 cgrms. of a preparation of metallic bismuth lasted in one case for 23 days after the last injection. The rate of elimination appears greatest for the camphocarbonate, and the maximum rate is usually observed 3 to 4 days after injection. Bismuth may also be excreted in the saliva, and 8 days after injection of 1 c.c. of a preparation of metallic bismuth traces were found in the saliva, blood and cephalic membrane of a syphilitic patient. Bismuth is, in fact, found in all the liquids of the organism, and the liver and kidneys appear to be the most retentive organs, the brain retaining but little. D. G. H.

Organic Analysis

Thionylaniline as an Organic Reagent and its use for Identifying Acids as Anilides. P. Carré and D. Libermann. (*Compt. rend.*, 1932, **194**, 2218–2220.)—Thionylaniline is readily produced with a good yield by the action of thionylchloride on aniline hydrochloride in benzene. Alcohols do not react with it, but many acids, on heating, form the corresponding anilides. The saturated fatty acids react readily; the aromatic acids yield only small quantities of the anilides, but give colour reactions. The presence of an unsaturated bond may interfere with the reaction, cinnamic acid, for example, giving a complicated reaction, with liberation of sulphur dioxide, hydrogen sulphide and resins. If, however, the unsaturated bond is sufficiently far removed from the acid radicle the reaction is not affected, so that oleic acid is transformed into anilide under the same conditions as the saturated fatty acids. Dibasic acids also react, oxalic, phthalic, succinic, glutaric and sebacic acids giving the corresponding anilides, but malonic acid yields only non-crystalline resinous products, and the reagent should not be used for this acid series. D. G. H.

Refractive Index of Tung Oil. J. Rinse. (*Rec. Trav. Chim. Pays-Bas*, 1932, **51**, 529–532.)—Krumbhaar's statement (*Chem.-Ztg.*, 1916, **40**, 937) that the refractive index of tung oil falls from 1·518 to 1·446 when the oil is heated for 4 hours at 200° C. is denied, a lowering to only 1·510 being observed; such lowering is not influenced by the acid value. Below 200° C. the rate of polymerisation of the oil is low. At higher temperatures the rate increases at first and decreases

before gelation occurs. When the oil is heated at various temperatures, ranging from 249° to 306° C., the final value of the refractive index is highest for the lowest temperature, the decrease being 0·0085 at 249° C. and 0·0109 at 306° C.; the times of gelation are 38 and 7·2 minutes, respectively. Addition of sulphur to the oil retards or prevents solidification, and the resulting oil differs markedly from the original oil, as it does not dry as quickly as the ordinary heated oil, and remains tacky for a long period. Polymerisation, caused by heating the oil in presence of a small proportion of sulphur as catalyst, is accompanied by a considerable heat effect. The mechanism of the action of sulphur is not understood, but possibly the double bonds are activated by the sulphur, giving a polymerised product quite different from that formed by the action of heat alone. T. H. P.

Inorganic Analysis

Use of Solid Cadmium Amalgam in Volumetric Analysis. S. Kaneko and C. Nemoto. (*J. Soc. Chem. Ind., Japan*, 1932, **35**, 185B.)—The solution to be reduced is treated with dilute sulphuric acid and 20 grms. of cadmium amalgam (15 per cent. Cd), and a little sodium carbonate to displace the air in the flask. The solution is warmed and shaken, the amalgam liquefying. When reduction is complete, the flask is cooled with a platinum wire inserted in contact with the amalgam, which adheres to the wire on solidifying and can thus be withdrawn. The technique was applied to the determination of iron in ferric alum and of molybdenum in ammonium molybdate. W. R. S.

Determination of Antimony in Copper and Copper Alloys. W. Boehm and W. Raetsch. (*Z. anal. Chem.*, 1932, **88**, 321–324.)—The customary procedure for the determination of minute quantities of antimony in copper, brass, and bronze consists in the addition of a little ferric alum to the nitrate solution and precipitation with excess of ammonia, the ferric hydroxide acting as a collector for the antimony (Brownson, *Z. angew. Chem.*, 1914, **27**, II, 83). The method was criticised by Blumenthal (*Z. anal. Chem.*, 1928, **74**, 33). The authors, however, were unable to detect any antimony by Blumenthal's permanganate method in the ammoniacal filtrates from iron precipitates obtained as above in the analysis of alloys. If, on the other hand, the process was carried out with pure copper solutions with addition of small amounts of potassium antimonate, the recovery of antimony was incomplete. Blumenthal's unfavourable opinion of the iron method is explained by the fact that he carried out his test analyses, not with antimony-bearing alloys, but with copper solutions to which small quantities of potassium antimonate had been added. The authors regard the iron method as reliable.
W. R. S.

Rapid Determination of Tin in Ferrotungsten and Wolframite. K. Kiefer. (*Z. anal. Chem.*, 1932, **88**, 243–249.)—The finely-powdered material (5 grms.) is fused with sodium peroxide in a steel crucible; the melt is dissolved in 150 c.c. of water, and transferred with a minimum of water to a measuring 500-c.c. flask. Strong hydrochloric acid (200 c.c.) is poured on top of the alkaline liquid, and the two layers are gradually mixed by shaking, when the bulk of the tungstic

acid thereby is precipitated in a pulverulent form. The higher chlorides of manganese are reduced with pure iron turnings, the solution is cooled, the volume adjusted, and the solution filtered. Two hundred c.c. of filtrate are transferred to a conical flask and treated, during cooling, with 1·3 grm. of fine aluminium powder. The liquid is heated to effect reduction and also complete solution of the aluminium, and treated, drop by drop, while hot, with a solution of 130 grms. of ferric chloride per litre of dilute hydrochloric acid, until the yellow colour of the ferric salt is distinctly recognisable. Tungstic acid is thus precipitated almost quantitatively. After 10 minutes' standing the solution is filtered through pulp, which is washed with hydrochloric acid (1:3). The filtrate is treated with 0·2 grm. of aluminium powder and 30 c.c. of strong hydrochloric acid, and the determination is concluded by the usual procedure for the titration of tin with iodine. The iodine solution must be standardised against tungsten ore or alloy, the tin-content of which has been accurately determined by Powell's method (*J. Soc. Chem. Ind.*, 1918, **37**, 285T), the iodine required being slightly in excess of the stoichiometric quantity. This is due to a little tungsten escaping precipitation. The time required for a determination is 2½ hours. W. R. S.

Use of the Antimony Electrode in the Electrometric Determination of Magnesium. B. B. Malvea and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1932, **54**, 2243–2247.)—Measured mixtures of solutions of magnesium and calcium chlorides of known strengths were diluted to 150 c.c. and acidified to methyl orange with dilute hydrochloric acid. The E.M.F. was then read, using a calomel half-cell and an antimony electrode prepared from commercial stick antimony sand-papered to a smooth surface; 0·1 or 1·0 *N* sodium hydroxide solution was added 0·2 c.c. at a time, 2 to 10 minutes being allowed in each case for the E.M.F. (E) to become constant. E was plotted against the alkali added (v), and the resulting curves showed two points of inflexion corresponding with the beginning and the end of the precipitation of magnesium hydroxide. The values of v at the actual points are best determined by plotting $\Delta E/\Delta v$ against v; the difference between the volumes corresponding with the two well-defined peaks of the curve thus obtained gives the alkali required to precipitate the magnesium. The method gives results agreeing well with those obtained by the hydrogen electrode, without the difficulties of manipulation, and it may be used for solutions containing eight to twenty-five times more calcium than magnesium. The minimum concentration is 0·1 grm. of MgO in 150 c.c., but at low dilutions an equivalent quantity of calcium produces unsatisfactory results. J. G.

Volumetric Determination of Sodium. N. H. Furman, E. R. Caley and I. C. Schoonover. (*J. Amer. Chem. Soc.*, 1932, **54**, 1344–1349.)—The method comprises the following steps: Precipitation of the sodium as sodium magnesium uranyl acetate, $NaMg(UO_2)_3(C_2H_3O_2)_9$; reduction of the uranium in the precipitate by metallic zinc (Jones's reductor); aeration of the solution to convert a small fraction of trivalent into tetravalent uranium; oxidation of the tetravalent to hexavalent uranium by a measured excess of standard ceric sulphate solution; potentiometric titration of the excess of ceric salt with ferrous sulphate. The

process is claimed to be advantageous for quantities of sodium not exceeding 0·01 grm. For manipulative details the original paper should be consulted. (*Cf.* ANALYST, 1931, **56**, 764; 1930, **55**, 527.) W. R. S.

Determination of Silica in Silicates. N. A. Tananaeff and F. I. Pertschik. (*Z. anal. Chem.*, 1932, **88**, 348–352.)—The determination is one by difference, the silica being converted into volatile fluoride and the residual fluorides converted into phosphates by successive treatment with oxalic acid and sodium metaphosphate. A determination can be carried out in 6 hours; an accuracy of about 0·2 per cent. is claimed. The silicate should contain less than 15 per cent. of alumina, otherwise high results are obtained. The sodium metaphosphate is made from pure microcosmic salt. This is heated in a platinum dish or crucible, finally over a blast burner, until the molten mass no longer evolves gas bubbles; the mass is poured out on to a clean metal plate, broken into small pieces, and kept in a desiccator for use. For the determination, one grm. of fine powder in a tared platinum crucible is moistened with water and attacked in the cold with 5 c.c. of hydrofluoric acid; the crucible is next placed on a water-bath, and the contents stirred with a platinum rod. More hydrofluoric acid is added if required. The liquid is evaporated to dryness and the residue intimately mixed with 2 grms. of finely-powdered oxalic acid. The covered crucible is heated in an oven at 120° C., and the temperature raised to 200° C., when the oxalic acid will be volatilised. The treatment with oxalic acid is repeated. An accurately weighed quantity of sodium metaphosphate (2 to 3 grms.) is added, and the crucible gently heated until the salt melts. Fusion is continued at higher temperature until constancy of weight is reached. The weight, less that of the crucible and the added metaphosphate, represents the oxides other than silica in the silicate. W. R. S.

Detection of the Acids of Arsenic and Phosphorus. N. A. Tananaeff and C. N. Potschinok. (*Z. anal. Chem.*, 1932, **88**, 271–278.)—A procedure is given for the detection of arsenic, arsenious, phosphoric, and phosphorous (hypophosphorous) acids in presence of each other and of other anions. The neutral or faintly alkaline solution is stirred and treated with 2 *N* ammonium chloride; any precipitate (silica) is filtered or centrifuged off, and the clear liquid is treated with magnesia mixture. The precipitate is collected, washed with dilute ammonia and dissolved in acetic acid, and the solution (2 c.c.) is divided into two portions: the first is treated with 0·5 to 1 c.c. of strong acetic acid and 0·1 *N* silver nitrate solution is added, drop by drop. A red-brown precipitate or coloration proves the presence of arsenic acid. The second portion is reduced with sodium sulphite and treated with 4 drops of nitric acid and ammonium molybdate; a yellow precipitate indicates phosphoric acid. The filtrate from the magnesium precipitate is oxidised with hydrogen peroxide; a fresh crystalline precipitate proves that arsenious or (hypo) phosphorous acid, or both, are present. The precipitate is collected and tested for arsenic and phosphorus as explained above. W. R. S.

Microchemical

Micro-analytical Methods in Industrial Laboratories. II. Pregl's Method of Combustion of Carbon and Hydrogen, without the use of Air. F. Vetter. (*Mikrochem.*, 1932, **10**, 109–113.)—Pregl's method is used unaltered for the combustion of an optimum amount of 3 to 5 mgrms. of material, with the exception that the absorption tubes are weighed full of oxygen instead of air. After the tube has been pre-heated in oxygen, the absorption tubes are attached, and oxygen is passed through the apparatus for ten minutes. The tubes are then left for ten minutes before being wiped and weighed. The combustion is made by the Pregl method, and takes ten minutes, after which, instead of air being passed through the tubes, the heating is continued for a further ten minutes (equivalent to 40 c.c. of oxygen) in a stream of oxygen. The tubes are then disconnected and weighed as before. Owing to the low rate of diffusion through the constrictions in the absorption tubes, results are obtained which are as accurate as when the original method is used. It is important that the constrictions and perforations in the absorption tubes should have the correct dimensions (constriction, 0·1 to 0·2 mm.; perforation, 0·2 to 0·3 mm.); otherwise inaccurate results are obtained. The advantages of the method are that the use of pure air is dispensed with, and this is of importance in a factory where the air is contaminated; also the time of analysis is shortened by 15 minutes. General precautions to remember in the analysis are:—(1) The weight of substance burnt should not be more than 5 mgrms., preferably 3 to 4 mgrms. (2) The movable wire gauze should never be omitted when heating with the movable burner. Silica tubes are unsuitable. (3) The rubber connection between the combustion tube and water-absorption tube should be left on the combustion tube between analyses, otherwise its hygroscopic properties cause errors. J. W. B.

Micro-analytical Methods in Industrial Laboratories. III. Micro-apparatus for the Gravimetric Determination of Water in Coal and other Solids. F. Vetter. (*Mikrochem.*, 1932, **10**, 407–408.)—The substance is heated to 110° C. in a boat in a short tube (10 cm. long) of Jena hard glass. The tube is heated by means of toluene vapour (or other suitable gas), which passes through an outer mantle which surrounds the tube. The water vapour to be weighed is carried over in a stream of an inert gas, such as nitrogen, into a Pregl absorption tube, containing calcium chloride, which is weighed full of nitrogen before and after the experiment. The nitrogen is passed through a pressure regulator, a bubble counter (so that the stream can be measured, as it should flow at 3 to 4 cm. per minute), then through calcium chloride, which should have the same vapour tension as that in the absorption tube, and, finally, through a tube with a glass stopper. This stopper is fitted outside the heating tube, to avoid contamination by lubricants. The exit end of the heating tube is drawn out to a tube of the same dimensions as the tip of the absorption tube, so that glass can touch glass inside the rubber connection. The absorption tube is connected with a Marriotte flask to regulate the flow of gases. The apparatus may also be used for drying under reduced pressure. This method is preferable to the methods in which the loss of

weight of the material is taken as the water-content, especially for hygroscopic substances which take up water appreciably, even when weighed in a boat in a stoppered bottle. J. W. B.

Micro-extraction Apparatus (for Examination of Paintings, etc.). H. Hetterich. (*Mikrochem.*, 1932, **10**, 379–383.)—A micro-extraction apparatus is designed which is suitable for separating the pigment and medium in the scientific examination of paintings. It consists of a small glass tube, 1 cm. in diameter, joined to a narrower tube, 1 cm. long and 0·4 cm. in diameter, sealed at the bottom. The solvent is placed in the narrow tube. The wider tube is 1·5 cm. long, and a small Gooch plate (0·6 cm. in diameter), with 15 perforations, rests on four projections of glass inside it, just above the narrow tube. The apparatus is fitted with a cork and condenser tube. The substance to be extracted is placed on a small filter paper, moistened with the solvent, placed flat on the Gooch plate, and held in position by a glass Gooch holder. The narrow tube containing the solvent is heated over the water-bath in a metal holder similar to that used by Emich for micro test tubes (*Recent Advances in Analytical Chemistry*, Vol. II, 1931, p. 324). An example is given of the extraction of the material used in an Ancient Egyptian wall painting. The sample was extracted for half-an-hour with chloroform, the solution was removed from the narrow tube with a fine capillary, and the medium used in the painting was then easily shown to be beeswax. After extraction the residue is also more easily identified. J. W. B.

Reviews

THE DONNAN EQUILIBRIA. By T. R. BOLAM, D.Sc. Pp. vii+154. London: G. Bell & Sons, Ltd. 1932. Price 9s.

As the result of the labours of many chemists, such as the late Jacques Loeb and the late Professor Procter, the so-called "Donnan equilibria" have been found to enter into many phenomena associated with the living process and with colloids generally. The interest thus aroused in this subject has been responsible for a considerable amount of research, particularly in more recent years. The present time is, therefore, fitting for the compilation of an adequate review of the existing literature, and this Dr. Bolam has very successfully done.

The volume consists of four chapters. In the first, there is developed the simple thermodynamic theory of the variations in osmotic pressure and electrical potential that occur at a membrane separating two solutions, one of which contains a non-diffusible ion. This follows the lines originally adopted by Professor Donnan, but, as the author states, they refer to ideal solutions only, and, in consequence, he has introduced the concept of "activity" in order that the Donnan Theory shall be of both general and strict application. The second chapter deals chiefly with the applications to general chemistry, though it is here that the fundamental work on gelatin and proteins is accorded brief discussion. Chapter III treats of some biological and technical applications, such as equilibria, occurring

in the blood and other body fluids, the nature of enzymes, the manufacture of leather (including the Procter–Wilson theory of swelling of gels), and dyeing. The last chapter, which is a short one, is devoted to certain applications which, at the present stage of development, are chiefly of physico-chemical interest, such as the use of Svedberg's "Ultracentrifuge" and the viscosity of protein solutions.

Throughout the book the matter has been admirably arranged, condensed and presented. It is just possible that in places the treatment is too sketchy, and a little more by way of explanation would have been an advantage to the general chemist. The book may be strongly recommended to all students preparing for special degrees in chemistry. It should also find a place in the library of older chemists who desire to know something of one of the more important trends of modern chemistry.

H. T. S. BRITTON

HYDROGEN IONS. THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY. By HUBERT T. S. BRITTON, D.Sc., F.I.C. Second Edition. Pp. xvi+589. London: Chapman & Hall. 1932. Price 25s.

There are few chemists to-day who, in one way or another, are not concerned with *p*H determinations; consequently the second edition of Dr. Britton's book will be welcomed by all. There have been no fundamental alterations in the character of the book, but, where necessary, fresh paragraphs have been introduced in order to bring the information completely up to date. The new work that has been published since the appearance of the first edition, two-and-a-half years ago, has necessitated increasing the size of the volume by nearly eighty pages.

The first fifteen chapters are devoted to the fundamental principles of the subject and the practical details for the determination of hydrogen ion concentrations by the potentiometric and colorimetric methods. As readers of the first edition will recollect, the facts are presented in a clear and simple manner, and the description of experimental methods is sufficiently precise to enable measurements to be undertaken without reference to the literature. Where further details are required, students will find that the references given in the text are both exhaustive and up-to-date. The section dealing with the measurement of E.M.F., employing thermionic valve circuits, has been considerably enlarged. The extremely small currents that are taken by valve circuits renders them very suitable for measuring the E.M.F. of cells that are readily polarised, or have an exceptionally high internal resistance, as is the case when a glass electrode is employed. It seems certain that the possibilities of such circuits will soon be more generally realised, and that they will be employed in preference to the Lindemann electrometer, which is generally used at the present time.

A serious weakness of the first edition was the omission of any mention of modern theories of electrolytes and, arising from this, the use of concentration terms in expressions where strictly the activities of the ions should have been employed. This defect has been largely overcome by the introduction of an extra chapter by Dr. R. A. Robinson on "Recent Theories of Electrolytic Solutions, the Influence of Neutral Salts." Useful summaries are given of the conception of affinity, the Debye-Hückel theory, and the experimental measurements of neutral salt effect. The limited space available does not permit anything more than a

bare outline of the modifications introduced by these theories to be given. However, in a textbook of applied science this is hardly a disadvantage, as the reader will not be confused by superfluous theory.

The latter half of the volume is devoted to a consideration of the importance of hydrogen-ion concentration in industrial and laboratory processes. Two new chapters are found here on "The Precipitation of Sulphides" and "The Hydrogen Ion Concentration of Hens' Eggs." These titles give a fair indication of the scope of this section of the book; there are seventeen chapters in which the importance of pH determinations in all branches of industry is dealt with. The book can be thoroughly recommended, and should find a place on the shelves of most libraries, whether private or public. R. H. PURCELL

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Fifth Edition. Edited by C. AINSWORTH MITCHELL, M.A., D.Sc., F.I.C. Vol. IX. Pp. 617. London: J. & A. Churchill. 1932. Price 32s.

All the volumes of "Allen" are full of good matter and are well-nigh indispensable to the analyst, but some contain more matter in everyday use than others. Volume IX is one of the most useful, and full of "meat" in more senses than one; those who deal with foodstuffs will find it invaluable, for no other single book, so far as the reviewer is aware, contains so much information on plant foods, plant proteins, milk, milk-products, cheese, meat, meat-products, eggs, fish and kindred topics. The contributors are Dr. Jordan Lloyd, Mr. Elsdon, Captain Golding, Mr. Bolton, and Dr. R. Moulton, all names well known in their respective spheres, and Dr. Mitchell has woven together their contributions with his accustomed skill. There is very much new matter in this volume: its bulk is increased by 113 pages, and most, but not quite all, obsolete matter has been excised, so it has not been possible, as had been intended, to complete the edition in nine volumes, and a tenth is in preparation, which will include, amongst other subjects, haemoglobin, scleroproteins, vitamins, woods, therapeutic-organic preparations, and a general index.

By far the most important sections here are those on milk, milk-products and meat-products. Mr. Elsdon, who has revised Dr. Van Slyke's former contribution, makes an excellent summary of the three principal milk proteins, dealing at length with casein, and briefly with albumin and globulin; the recent work of Moir is included. Capt. Golding deals all too briefly with milk, its variations, analysis and adulteration; he outlines the freezing-point method for detecting added water, but one could wish he had dealt more fully with this thorny problem, and given a clear opinion on all the available methods. The detection and significance of nitrates have unfortunately been omitted; also, there is no mention of the analysis of altered or sour milk; this problem, though quite old, is still with us, and the accepted methods ought to be described. The subject of graded milk comes within the purview of the analyst, and needs description and discussion of methods of testing.

Mr. Bolton deals very thoroughly with milk-products, and besides the well-known ones, such as cream, condensed milk and cheese, gives useful information on many interesting, if recondite, points; where else can the analyst find all about

mazum and yoghourt? One would like to draw him out more fully on infant foods and the analysis of pasteurised cheese. Van Slyke's book on cheese is unfortunately omitted in the bibliography (on cheese), and it is the best. It is sad to observe that 23 countries have legislative standards for cheese, but England still has none.

The largest section deals with meat-products, and this is admirably done. There are up-to-date tables of composition of the different kinds of meats, including their mineral constituents; the identification of different species of meat used for food by serological methods is well, but briefly, described, as are also their microscopical characteristics. In this connection it is odd that of the eight illustrations of muscle fibres, four are human and three others muscle of a dog, frog and wasp; for the ox, sheep, etc., we are referred to "Meat through the Microscope." Details are given of the best methods for examining meat extracts and of supposed unsound meat products, also pickled and cured meats and sausages. Metallic contamination, colouring matters and preservatives and their determination are well described.

About forty pages are devoted to eggs, both fresh and dried, and give valuable data not found in most other books; the section concludes with twenty pages on fish. Altogether, this is an excellent contribution.

Quite naturally one might comment on details of omission or many small points, but sufficient has been said to indicate that the volume, as a whole, is excellent, and one of the most useful of the series. Volume X will be awaited with interest.

Alfred H. Allen died in 1904, but "Allen" is still living and going strong in 1932.

H. E. Cox

STRUCTURE AND COMPOSITION OF FOODS. By ANDREW L. WINTON, Ph.D., and KATE BARBER WINTON, Ph.D. Volume I. CEREALS, NUTS AND OIL SEEDS. Pp. 710. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1932. Price 53s. net.

No one will underrate the importance of a work on the ambitious scale of "Structure and Composition of Foods," of which Volume I ("Cereals, Nuts, and Oil Seeds") is under review. Moreover, from the point of view of microscopy, any work by Winton is acceptable and authoritative. The authors' task, to quote from the preface, has been ". . . partly to collect, select, summarise, and unify, so far as expedient, results . . . scattered through numerous journals, and partly to add their own contributions, largely hitherto unpublished, on the gross and microscopic structure. . . ." The method of treatment is particularly interesting, the scientific matter being considered under three main heads: (1) Macroscopic structure, (2) microscopic structure, (3) chemical composition. "The chief mission of the work," the authors state, is "the exploiting of the interrelation of structure or optical science to composition or chemical science." For the macroscopic and microscopic sections, all praise is due to the authors; their descriptions are clear, the choice and reproductions of sketches and photomicrographs excellent, and these alone well justify the book—although its price of 53s. appears to be very high. For the collection of chemical data, the thanks of everyone working in this field are due, but it appears to be regrettable that the

authors have thought fit to discuss the chemical aspect, for it can only be concluded from statements made, that they have little intimate knowledge of the questions discussed. As an example, the following statement appears on p. 214: "The low results by the open dish method (for moisture in flour) . . . are partly but not completely nor uniformly, compensated for by the use of the conventional factor 6·25, instead of the more accurate factor 5·70" . . . the scientific connection between low moisture results and the alteration of the factor for converting nitrogen to protein being difficult to follow.

Nitrogen-free extract is a very vague term, as applied by the authors. For example, "The oat bran is the true bran of oat-groats from which the starch has been removed by washing . . . Rolled Oats, N-f-ext 65·57 per cent.; Oat bran, N-f-ext 59·90 per cent." The authors make a claim for a kind of contracted word to represent "Nitrogen-free extract." "The authors (p. 10) in their notes and conversation have adopted 'nifext'—nineteen letters, a hyphen, and a space reduced to six letters—the derivation and meaning of which should be evident even to a foreign reader. The writers, hesitating to go to the full limit in this work, have employed in table-heads the abbreviated form 'N-f-ext,' but hope that this will be a stepping-stone to the coined word 'nifext'." It is to be hoped that such will not happen, or we may look forward to "sonofts" in dairy chemistry, and to "Fafres," as representing "Fat-free-residue."

One is forced, however, to the conclusion that the book is not meant for chemists, for definitions are given which are distinctly loosely worded, *e.g.* (p. 358): "The saponification number is a measure of molecular weight or the number of carbon atoms in the acid molecule. . . ."

On p. 17, too, the statement is made, referring to the ash of plants: "When neither the content of carbon dioxide nor alkalinity of ash is given, the reader *must make a laborious calculation* in order to determine whether the ash is neutral or alkaline." (The italics are the reviewer's.)

The elements of microscopy are so widely learned by English students that the following appears to be somewhat redundant: "To chemists and others who are unfamiliar with micro-technique, and who are afflicted with a kind of 'stage fright,' it may be said that the microscope is little more complicated or difficult to operate than the opera-glass."

Notwithstanding the fact that to the chemist reading the book such points, mis-statements and loosely worded definitions as those quoted are irritating, the book is a valuable compendium of fact—apart from the opinions of the authors, and accordingly is worthy of a place on our bookshelves. L. H. LAMPITT

MONOGRAPHS ON BIOCHEMISTRY. ALCOHOLIC FERMENTATION. By Prof. ARTHUR HARDEN, F.R.S., etc. Fourth Edition. Pp. vii+243, with illustrations. London and New York: Longmans, Green & Co. 1932. Price 15s. net.

The production of ethyl alcohol by a process, termed at a very early date "fermentation" is one of the oldest chemical problems to be studied, and, in modern science, it has proved to be one of the most suggestive of all those connected with biochemistry.

The history of alcoholic fermentation may be divided into three epochs, when

chemical, biological, and biochemical theories were put forward. The first was that propounded by Willis in 1659 and by Stahl in 1697. It was developed by Liebig a hundred years later. The second was placed on an irrefutable footing by Pasteur, whilst the third had its birth in the discovery of E. Buchner, that alcoholic fermentation is due to an enzyme which can be separated from yeast. Those who are familiar with the literature of the subject from the time of Buchner's great discovery will place Professor Arthur Harden in the front rank of investigators in this domain, for he, with his school, has done more to develop our knowledge of alcoholic fermentation than any other chemist of recent times.

In the nine years since the last edition of this monograph was published, a large number of papers on the subject have appeared. To the present edition 49 additional pages have been added, but the number of chapters remains the same, and the headings have not been altered.

The first two chapters, the text of which is historical, have received no revision, but the remaining eight chapters have been considerably extended and brought up-to-date.

The different enzymes of yeast, besides zymase and sucrase, are described, such as carboxylase, carboligase, and the reducing enzymes. It is stated that up to the present the following enzymes and complex substances concerned with oxidation and reduction have been detected in the yeast cell: glutathione, a dehydrogenase, a thermostable peroxidase, an indophenol oxidase, and a cytochrome system containing, as shown by Keilin, three components.

The function of phosphates in alcoholic fermentation is dealt with at length, as are also the chemical changes involved in fermentation and the mechanism of fermentation. The views of different authors on these subjects are extremely conflicting.

The accelerating action of phosphates and arsenates on the fermentation of sugars by zymase preparations was first observed by Harden and his colleagues, and this led to the discovery of the sugar phosphates. When glucose, mannose, fructose, or sucrose is fermented with yeast preparations in presence of phosphates, three well-defined compounds may be isolated: a hexose diphosphate (Harden and Young), a hexosemonophosphate (Harden and Robison), and a trehalosemonophosphate (Robison and Morgan). Neuberg has obtained a second hexosemonophosphate by the partial hydrolysis of the diphosphate. It is a much less stable substance than the monophosphate formed direct, and Meyerhof suggests that such an active phosphate is the first product to be formed in alcoholic fermentation. It seems to be well established from the work of Robison and Morgan that the diphosphate is a derivative of γ-fructose. It has not been found possible to isolate corresponding arsenates.

The chemical changes involved in fermentation are discussed at length, but the views held by different workers are here also conflicting. Whilst the book deals mainly with acellular fermentation, that brought about by the living cell is also discussed.

Those who expect to be able to use this monograph as a teaching book for elementary students may be disappointed, for the subject is all to complicated to

be treated fully within the limits of space available. It is, however, a complete guide to the literature, and as such will be found invaluable by research workers and teachers.

ARTHUR R. LING

DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. Vol. IV. SENAPA TO ZUCCHERO. By Professor G. VITTORIO VILLAVECCHIA AND OTHERS. Fifth Edition, revised and enlarged. Milan: Ulrico Hoepli. 1932. Price 80 lire.

This volume, which completes the work (see THE ANALYST, 1930, 55, 357; 1932, 69), contains 460 pages of text, and includes, among its contents, articles dealing with various subjects in which Italy is particularly interested, such as silk (48 pages), silk fabrics, grapes, wine (37 pages), sulphur (11 pages), etc. As in the preceding three volumes, the materials considered cover a wide range, scarcely anything of interest to industrial chemists or to dealers in, or manufacturers of, chemical products, being omitted. In addition to those which may be defined more strictly as chemical in nature, the products treated of in the present volume comprise mustard, sepia, sesamé oil, tallow, medicinal syrups and medicinal substances in general, emery, soya bean oil, solvents and plasticisers for lacquers, sumac, spices, sponges, rags, ostrich feathers, cork, suppositories, tobacco, tannins, truffles, tea, fuller's and other earths, waterproof fabrics, tinctures, hair dyes, turpentine, eggs, glass, saffron, civet, pumpkins, and a host of others. For each of these, the occurrence, preparation, and uses are described, and trade statistics are given.

The volume is completed by an index to the whole work, this containing not merely the names of the principal headings in each of five languages—Italian, French, German, English and Spanish—but, in addition, the Italian names of the very large number of substances referred to in the text of the articles. The fact that it extends to 280 pages, each of three columns, and comprises upwards of 50,000 entries, will give an indication of the exhaustive character of the index and of its great value to users of the book.

Probably no other single publication in any language furnishes such a mass of similar information, and any analyst with a general practice and with an elementary knowledge of the Italian language, would frequently find reference to its pages of advantage.

The cost of the four volumes amounts to only 260 lire or, at the existing rate of exchange, about £3 13s., which is only a fraction of the price of German or American, or even English, scientific books of corresponding magnitude. A small increase in this very moderate figure would have allowed these heavy volumes to be bound in good stiff covers, the thin card ones supplied being quite inadequate for books likely to be in daily use.

The appended list of corrigenda for the four volumes requires further slight correction in a few particulars.

T. H. POPE