DECEMBER, 1935 Vol. 60, No. 717

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 6th, the President, Mr. John Evans, M.Sc., F.I.C., being in the chair.

Certificates were read in favour of Kenneth Franklyn Allen, B.Sc., Vincent Anthony Cachia, B.Sc., A.I.C., Alfred Randolph Campbell, F.I.C., Philip Farrugia, B.Sc., M.D., George Eric Forstner, M.Sc., A.I.C., Harry Richard Knight, A.I.C., A.R.S.M., William George Mitchell, Theodore Lawrence Parkinson, B.Sc., A.I.C., Herbert Stanley Redgrove, B.Sc., F.I.C., Herbert Newton Wilson, F.I.C., William Wilson, F.I.C.

The following were elected Members of the Society:—William Reginald Bage, Albert R. Bonham, B.A.Sc., F.C.I.C., Henri Charles Philip Chapleau, B.A.Sc., Leo Cooksey, B.Sc., F.I.C., Douglas Eric Davis, B.Sc., F.I.C., Frederick Ellington, B.Sc., A.R.C.S., A.I.C., Edward Oscar Heinrich, B.S., James Arthur Durham Hickson, B.Sc., A.I.C., Donald Robert Jackson, Daniel Carswell Macpherson, B.Sc., Florence Ellen Murphy, B.Sc., Temple Clifford John Ovenston, B.Sc., Ph.D., A.I.C., George Herbert Stott, M.Sc., F.I.C., Basil C. L. Summers, B.Sc., Stanley Gordon Willimott, B.Sc., Ph.D., A.I.C.

The following papers were read and discussed:—"Characteristics of Halibut Liver Oils," by R. T. M. Haines, M.A., and J. C. Drummond, D.Sc., F.I.C.; "Notes on Mendel and Goldschieder's Method for Determining Lactic Acid in Blood," by R. Milton, B.Sc.; "The Application of Controlled Potential to Microchemical Analysis," by A. J. Lindsey, M.Sc., A.I.C., and H. J. S. Sand, D.Sc., Ph.D., F.I.C.; and "The Micro-Electrolytic Determination of Bismuth and Lead and their Separation by Graded Potential," by A. J. Lindsey, M.Sc., A.I.C.

SCOTTISH SECTION

THE opening meeting of the Section was held in Glasgow on November 13th, 1935, Mr. R. T. Thomson, F.I.C., being in the chair. Dr. T. W. Drinkwater, Vice-Chairman of the Section, was unable to be present owing to illness. Sixteen members attended.

The Section was honoured by the presence of Mr. John Evans, M.Sc., F.I.C., President of the Society; Dr. G. Roche Lynch, Hon. Secretary; Dr. E. B.

Hughes, Hon. Treasurer; and Professor W. H. Roberts, Chairman of the North of England Section.

Apologies for absence were intimated from Dr. C. Ainsworth Mitchell, Dr. T. W. Drinkwater, Mr. T. Cockburn and Professor J. Hendrick.

The following papers were read and discussed:—"Some Properties of Sodium Hexametaphosphate," by R. T. Thomson, F.I.C.; and "The Determination of Iodine in Kelp," by J. B. McKean, F.I.C.

Obituary

SAMUEL FRANCIS BURFORD

On 29th August Samuel Burford passed away at the home of his son at Rickmansworth. He had reached the good age of 78 years, and his death deprives the Society of another old and very loyal member.

Originally intended for the printing trade, Burford early interested himself in pharmacy, and passed the Major Examination of the Pharmaceutical Society in 1883. He subsequently continued the study of analytical chemistry under Dr. John Muter in London. In 1892 he started a practice as an analytical and consulting chemist in Leicester, and in the same year joined the Society of Public Analysts, being elected a Vice-President in 1924–1925. He was also for many years a member of the Chemical Society, and in 1918 was elected a Fellow of the Institute of Chemistry.

As part of his practice, he acted as chemist to the Corporation sewage, water and other departments, and in 1913 was appointed Public Analyst for Leicester. The post was originally a part-time one, but was constituted a whole-time appointment in 1925 on the construction of the City Laboratory. He retired from practice in 1929.

In the course of a busy career Burford found time for many activities outside his profession. He was recently President of the Leicester and Leicestershire Chemists' Association for two or three years, a position he gave up only from ill-health just before his death. He had also been a member of the Highfields Hospital Committee since its foundation, and Honorary Secretary since 1918.

He was well known in Free Church circles, and had been on the executive of the Leicester Free Church Council for many years. At one time a lay preacher, he was always an active worker in his own circle, and his services could always be relied upon for a worthy cause. He took an active part in adult school work, and was recently elected President of the Leicestershire and Rutland Band of Hope Union after having been a vice-president for many years.

His character was one of great kindliness; his simplicity of manner and evident honesty of purpose endeared him to those about him. A life-long abstainer and non-smoker, he was yet blessed with a spirit of tolerance and a keen sense of humour that made him very human.

He outlived his wife by less than a month, and leaves a son, a daughter and two grandchildren, to all of whom the sympathy of the Society is extended. At his funeral the Society was represented by the writer. F. C. Bullock

The Chemical Examination of Furs in Relation to Dermatitis

Part VI. The Identification of Vegetable and Other Dyes

By H. E. COX, D.Sc., Ph.D., F.I.C.

(*Read at the Meeting, October* 2, 1935)

An experience ranging over several hundred cases of alleged fur dermatitis shows that this disease rarely arises from the common vegetable dyestuffs used on fur. It is true that a few such cases have been recorded, but in some of these it may be doubted whether the real identity of the irritant substances was adequately determined; for it is desirable to find out not only what is present but also what is absent. I have shown in an earlier paper[1] that in the great majority of cases the nocuous substance has been found to be an amino compound in an unoxidised or partly oxidised state. In order to get any understanding of the physiological causes of skin irritation in connection with dyes it is essential to accumulate accurate data as to the constitution of substances which are irritant and those which are not; this pre-supposes analytical diagnosis of the pigment and proof that the particular dyestuff, and no other, is present. The analytical recognition of fur dyes—or hair dyes—is often a difficult matter. Complications are caused by the fact that in any given case there may be two vegetable dyes with or without an oxidation dye, and the reactions of the vegetable dyes are complicated by the presence of the mordant and of various tannins and other substances which may be extracted from the fur fibres. Occasionally, mineral pigments are used.

The number of vegetable dyes known to be used on furs is not very large, but by the skilful use of mordants a wide range of colours is obtainable. Besides those used on fur, there are a few others used as hair dyes which I have included in this section; there is no real difference between a hair dye and a fur dye, and it is common to both that they must be applied at quite low temperatures and without strong acid or alkali. The number of possible oxidation dyes is legion. It is true that about a dozen are in common use, but some hundreds have been described or patented in recent years, and it is impracticable to devise a scheme which would cover all the possibilities. It is proposed to describe the chemical nature and reactions of the principal vegetable dyes which are met in practice and a scheme of analysis which will often suffice to discover with what substance or substances fur or hair has been dyed. It should be clearly stated that no scheme can cover all types, and that more than one substance may be met in any given case. The topping of vegetable colours with an oxidation colour is common practice, either for improving the shade or lustre of a fur or for levelling up the colour of a composite garment. There are reasons for thinking that in some of the reported cases of vegetable dyes an oxidation dye was really present as a "topping." The very common case of diamines on logwood has been considered in Part V of this series.[2]

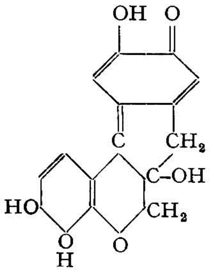
SOME PROPERTIES OF UNDYED FUR.—Undyed fur as it appears in commerce is peculiarly resistant to chemical agents. Three factors seem to contribute to this: one, the high resistance of the keratinoid fibres in which the pigment is encased; two, the nature of the pigment itself, about which so little is known; and three, the processes of curing which the pelt has undergone at the hands of the fur dresser. Animal hair is, in general, coarser and more resistant to bleaching agents than is human hair, which, as everyone knows, is easily bleached by peroxide. Furs are slowly bleached in acid solution by sulphur dioxide, but they yield more readily to oxidising agents such as permanganate, hypochlorite or hydrogen peroxide in weak alkaline solution. In dyed furs the dye is largely on, or near, the surface of the fibres, so that it is more quickly bleached than the natural colours, which are mainly inside the fibre. The nature of the pigment in animal or human hair is unknown; possibly it varies in different species. It is generally fat-soluble, and is thought to be an oxidation product of amino-compounds such as tyrosine, effected by tyrosinase or other natural enzymes. Microscopic examination shows that the pigment is distributed in granules in the medulla; the size and frequency of the granules are influenced by climate, season and food, as well as by the species of animal. These colour granules gradually diffuse outward into the fibre itself, but even there they are protected by the keratin and the film of oil, which prevent the penetration of watery reagents unless an alkali is added. It is well known in the trade that the hair of animals from wet districts contains more pigment than that of the same species in dry places. The lipoid nature of the pigment appears to be related to the water-resisting properties of the fur. Also, the process of rolling or calendering, commonly employed to give lustre, makes the fur more resistant. When fur has been dyed by a dipping method the pelt is stained, and inspection discloses the fact; this simple observation of course fails to reveal evidence of the common process of brush dyeing.

As an alkaline solution of hydrogen peroxide ultimately destroys the colour both of dyed and undyed fur, it is not really useful as a reagent for testing purposes. Sodium formaldehyde sulphoxylate ($NaHSO_2.HCHO.2H_2O$), however, reduces most artificial dyes quickly, but does not markedly bleach an undyed fur in a short time; it is therefore quite useful as a differential reagent. Hot dilute hydrochloric acid has very little action on the colour of natural hair; the fibre is, of course, weakened, and various nitrogenous substances, with little of the vegetable pigment, are extracted. On the other hand, nearly all the artificial pigments are either extracted or decomposed by such treatment, so that one gets a solution of the dye, complicated, of course, by the presence of tannins and keratin products.

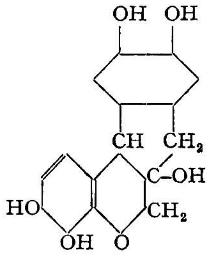
Heavy or dark dyeings are easily recognised, but the lighter shades, tinting and topping, often present difficulties.

VEGETABLE DYES COMMONLY USED ON FURS.—It is necessary to consider in detail the nature and chemical constitution of the substances used as dyes, not only for the sake of finding their reactions, but for the more important object of considering their possible action on the skin, and in what way they differ from dyes or intermediates known to be irritant. The following vegetable substances are common on furs: logwood (including brazil wood), quercitrin (black oak), flavin, fustic, catechu and similar tannins, gall-nuts, occasionally turmeric, and, for hair, henna. Each of these substances may be combined with iron, copper, chromium, aluminium or other metal as mordant, and the shade of the dyed fur is dependent as much on the mordant as on the dyestuff. Hence the ash of the hair should be examined for metals, in view of the fact that iron will always be found and traces of other metals may be present from natural causes. Lead, silver, mercury and bismuth are sometimes used in the form of mineral pigments.

Logwood.—This well-known dye wood has been in use in England for about 400 years,[3] though it was at one time put under a ban by Queen Elizabeth. This ban had nothing to do with dermatitis, but was due to the failure of the dyers of those days to use it properly so as to get good permanent results. Charles II removed the prohibition, and, since then, the dye has enjoyed a deservedly high reputation, alike for excellence of colour, permanence and harmlessness. It was included in the early editions of the London Pharmacopoeia. The colouring matter of *Haematoxylon campechianum* is haematoxylin, which is the leuco compound of the true dyestuff haematin. Brazil wood (*Caesalpinia sappan*) contains a methyl ether of haematoxylin, which yields this substance on oxidation. It has been shown by the work of Perkin, Robinson[4] and others that haematoxylin and haematin contain a di-hydro-pyran group, and have the structures:



Haematin

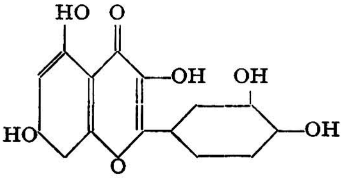


Haematoxylin

These compounds, and also brazilein, are converted into red salts when boiled with mineral acid, and their original colour cannot readily be restored. The red colour is slowly reduced by hydrogen. Sulphur dioxide forms a colourless compound by addition, not by reduction. Alkalis give a crimson colour with brazil wood, violet with logwood; ferric chloride gives deep brown or purple-black, and lead acetate a pink or blue precipitate, respectively. The red colour is destroyed by reduction with zinc or tin in acid solution, and is restored by exposure to the air; the reduced solution gives no indamine reaction and no diazo compound. These facts are useful in a search for admixed oxidation colours. Alum gives a rose-red lake, and pyrogallol, for which a delicate test is available, may be formed by fusion with alkali.

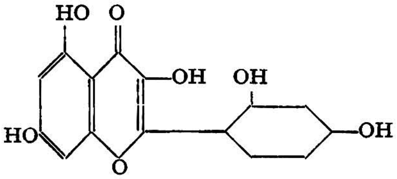
Logwood is usually met with in dark brown or black dyed furs mordanted with copper or iron, and may be stripped by boiling with dilute hydrochloric acid.

Quercitrin is another wood dye whose history goes back about 250 years. The dye is obtained from black oak, in which it occurs as the glucoside, quercitrin, which, on hydrolysis, yields the flavone dye, quercetin, having the constitution (Perkin[5]):



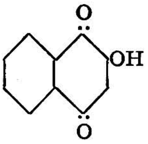
Flavin is a commercial preparation of quercitrin and yields stronger colours than does the bark itself. It dyes fur brown with chromium, orange with aluminium, yellow with tin, and olive with iron as mordant. Quercitrin gives a yellow precipitate with lead acetate. It should be noted that the OH groups in the flavone ring are at the 3′, 4′ positions; Robinson has shown that addition of ferric chloride to an alcoholic solution of anthocyanins or anthocyanidins containing OH groups in these positions gives a blue colour, becoming violet on the addition of water. Dilute aqueous solutions give no diazo reaction, but a slight brown indamine colour.

Fustic (old fustic), the wood of *Chlorophora tinctoria,* contains another flavonol derivative, morin, which is closely allied to quercetin. Kostanecki and others[6] give it the structure:



It dyes furs thus:—With chromium, olive yellow; aluminium, yellow; tin, yellow; iron, deep brown; it is much used in conjunction with other colours to produce brown and drab shades. In solution it forms an orange precipitate with lead acetate and an olive green with ferric chloride; with nitrite it gives a dark colour intensified by alkali, and with diazobenzene chloride a yellow dye. The indamine reaction is negative. Fusion with alkali yields both phloroglucinol and resorcinol.

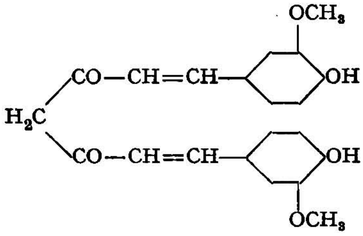
Henna.—This well-known hair dye is used but seldom on furs, though its use for hair and nails dates back to the days of the Pharaohs, a time, we are told, when dyed finger and toe nails were not confined to the young and fashionable, but were common to all women. The active principle of the leaves (of *Lawsonia alba*) is lawsone, which is probably identical with 2-hydroxy 1 : 4 naphthaquinone,[7,8]



and has m.p. 192–195° C., though some other substances are present also. I dyes hair or wool an orange-yellow, which is intensified by ammonia, but is no very permanent. The colour is extractable from aqueous solutions by ether if sufficient colouring matter is available, henna may be recognised by the stron absorption band of an amyl alcohol extract at 656–670$m\mu$. When considering its chemical reactions it should be remembered that commercial henna powders frequently contain pyrogallol, and often a metallic salt or even an amino compound. An alcoholic solution gives a red colour with nickel acetate, or an orange colour with copper acetate. Aqueous solutions show:

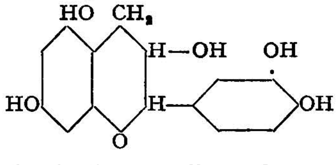
With ferric chloride — a greenish liquid which should not give a black colour when poured into excess of dilute ammonia (absence of pyrogallol).
Indamine test — negative.
Sodium nitrite — no colour.
Diazobenzene — a red colour or precipitate, yellow if very dilute.
Heated with zinc dust — no red colour.

Turmeric, the rhizome of *Curcuma longa*, affords another well-known yellow pigment, curcumin, which is much used in India and a little in England as a hair dye, rather than for furs. It is employed sometimes as a direct dye, but more usually with a mordant in place of fustic. The colour is not resistant to light or alkalis. With chromium, the colour is brown; aluminium, yellow; tin, orange; and iron, a brownish-black. The structure of the dye, according to Kostanecki[9] and Rupe,[10] is:



When the dye is dissolved in concentrated sulphuric acid the colour is bright red, a fact which provides a direct test on hair or fur. Lead acetate gives a yellowish precipitate. The familiar reaction with boric acid in acid solution is due to the formation of rosocyanin, which is isomeric with curcumin and forms characteristic blue-green salts with potash or ammonia. Turmeric gives but little colour with ferric chloride, is not diazotised by nitrite, and forms no indamine. Alcoholic or ethereal extracts show a green fluorescence.

Catechu, or cutch, is much used for some types of fur. The colouring matter, catechin, belongs to the coumarone group, and exists in dextro and laevo forms. According to Mason,[11] the *d*-variety has the structure



Mordanted with iron, fur is dyed a brown-olive colour. The solution gives a deep green colour with ferric chloride, a white precipitate with lead acetate, and, when oxidised with dilute ferricyanide in presence of potassium acetate, an orange precipitate. On addition of concentrated sulphuric acid to a hot acetic acid solution of catechin, an orange-red powder—the characteristic phlobaphen—separates. Mitchell's ferrous tartrate reagent gives no characteristic colour, but hydrochloric acid and sodium nitrite give a dark brown, and the product, like that of some other tannins, coupled with alkaline β-naphthol, is deep red. There is no indamine reaction—other than the ferric chloride colour. A match-stick with hydrochloric acid gives the phloroglucinol colour.

Gall Nuts and Oak-bark.—The various forms of gallotannic or quercitannic acid are much used on certain types of grey fur, such as squirrel or moleskin. These, and some other tannins, cannot usually be separately identified on the fur. A well-known black is produced from gall nuts and sumach mordanted with sulphate of iron and copper in the presence of litharge and alum. These tannins give marked colours with Mitchell's ferrous tartrate reagent. Ferric chloride shows a brownish-green with quercitannic acid and blue-black with gallotannins. The indamine reaction is negative, but nitrite gives a brown colour which is intensified when coupled with alkaline β-naphthol. Bromine produces a yellowish-white precipitate.

Pyrogallol, obtained from gallic acid, is also much used on grey furs, such as squirrel. Some of its reactions in dilute solution have been given in an earlier paper of this series.

Further details of the many identification reactions of the tannins are given in Vol. V of *Allen's Commercial Organic Analysis*, so that it is unnecessary to amplify them here.

It will be noticed that all the foregoing natural pigments, though of varying types, have it in common that they are non-nitrogenous, whereas the usual oxidation bases all depend upon nitrogen groups for their activity. Most of the textile dyes which arise in this connection are likewise nitrogenous. The analysis of dyed furs is complicated by the fact that some nitrogen is always extracted by water or solvents, and that many of the tannins (which are so commonly present) give coloured oxidation products, react with sodium nitrite, and, when coupled with alkaline naphthol sulphonic acids, give colours simulating the diazo reaction. Also, some tannins give a pseudo-indamine reaction, so that a green indamine must not be taken as necessarily indicating a diamine.

The following tables show a simple, but not exhaustive, scheme which will usually indicate the nature of any artificial dyestuff present on a fur. The tests are conveniently applied in ordinary test-tubes to small clippings of the hair.

TABLE A

Boil the fur fibre with dilute hydrochloric acid (1:10)

Fur unaffected; liquor not coloured	Fur reddened; liquor bright red	Fur partly bleached; liquor not coloured	Fur not much changed		
			Liquor dark brown	Liquor yellow	Liquor greenish
1	2	3	4	5	6
Undyed fur	Logwood Brazil wood and some oxidation colours	Metallic pigments: Lead Silver Bismuth	Oxidation colours: Aniline black. Also cutch with Cu or Cr	Turmeric Henna Fustic Quercitrin	Tannins Oak-bark Gall nuts. Liquor nearly colourless: Pyrogallol

They should be applied to several pieces taken from any differently coloured parts; the leather should not be included, or misleading results are likely to be obtained from the various leather extractives.[12] The method follows the plan adopted by A. G. Green in his work on *Analysis of Dyestuffs*, which is so useful for the identification of the older types of textile colours.

TABLE B

Boil for half a minute with sodium formaldehyde-sulphoxylate solution*

The fibre is unaffected	Fibre slightly bleached	Fibre much bleached		
1	2	3. Oxidation colours from amines, etc. Turmeric, henna Many textile dyes, such as:		
Undyed fur Aniline black Cutch is almost unaffected	Fustic Quercitrin Flavine Tannins	4	5	6
		Azines. Colour restored on exposure to air	Triphenylmethane colours. Restored by persulphate	Nitro and azo colours. Not restored by air or persulphate

* This solution is prepared according to the formula of A. G. Green:—Dissolve 50 g. of sodium formaldehyde-sulphoxylate in 150 ml. of hot water; grind 0·25 g. of precipitated anthraquinone into a paste with some of this solution, then dilute the whole to 500 ml. The solution should be practically neutral, not acid.

Notes.—A (1). Observe if the pelt is unstained.

A (2). The acid extract from logwood and the other red woods gives characteristic blue or violet colours with alum and ammonia, whereas oxidation colours give only brown or black. Make the acid extract nearly neutral with chalk, add a little zinc dust, and filter; then apply the indamine reaction. The resulting colour varies somewhat with the concentration, but may be:

TABLE A (2)

Blue-green	Brown-pink	
p-Phenylenediamine *p*-Tolylenediamine *p.p'*-Diamino-diphenylamine, etc.	Meta-diamines *o*-Amino-phenol *m*-Amino-phenol, etc.	*p*-Amino phenol 2:4-Diamino-phenol Dimethyl-*p*-phenylenediamine *p*-Aminodiphenylamine, etc.

A (3). Lead sulphide, mercury sulphide, silver or bismuth compounds may be detected here; identify in the ordinary way.

A (4). Test for oxidation colours as in A (2). Cutch gives a dirty green colour with ferric chloride, and gives the diazo reaction; confirm by the reactions given on p. 797.

A (5). The colour will be darkened on adding ammonia; recognised by the boric acid reaction. Henna can be identified by the red colour it gives in alcoholic solution with nickel acetate. Fustic is indicated by the formation of a yellow dye with diazobenzene, and of an orange precipitate with lead acetate in neutral solution. Quercitrin gives a negative diazo reaction and the other tests as shown on p. 796.

A (6). Make the solution nearly neutral and add

(*a*) One per cent. iron alum solution; a purple or black colour indicates a catechol tannin.

(*b*) Mitchell's ferrous tartrate reagent: gallotannins (and a few anthocyanins) give a blue-black colour; ellagitannins show only a dirty green.

(*c*) Ferric chloride, and pour into excess of very dilute ammonia: pyrogallol gives a black colour.

If sufficient material is available, the goldbeaters' skin test is applied; it is specific for tannins.

B. The effect of boiling with a reducing solution, such as this, is one of degree; nearly all the furs are partially bleached on prolonged boiling, so that it is important not to continue too long. The coarser types of hair are more resistant than the small soft varieties.

B (1). Some mineral pigments, such as lead sulphide, will also be unaltered. Indications of these or of aniline black will be obtained by the acid boiling.

B (2). The resistance of these varies somewhat according to the mordant; acid treatment strips them quickly.

B (3). A mordant is usually present with the oxidation colours; the reduction process gives rise to an amine in most cases, but not always the original amine.

B (4, 5 and 6). Textile dyes, such as these, can usually be applied only at high temperatures which cannot be used with furs unless they have previously been chrome-tanned, *e.g.* some seal skins. Examine the pelt for substantial quantities of chromium. If textile dyes are present, the methods described by Green should be used.

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DISCUSSION

Mr. C. E. SAGE had hoped to hear from Dr. Cox whether there were any particular dangers attached to the use of vegetable dyes. His own experience with logwood over many years showed that it was not harmful, and the irritation it sometimes caused was only what was to be expected from the dusty particles. The pigments from some berries caused irritation between the fingers of the work-people, and archil gave rise to complaints occasionally, but whether that was due to the pigment or to the method of its preparation, was not known.

Mr. H. S. REDGROVE said that he would like to express appreciation of Dr. Cox's paper, because his own interest centred in dyes used for living hair, and he did feel that the chemistry of hair dyes needed exploring and clearing up. He and the late Mr. Foan had made some efforts to shed light on this subject, but there was an enormous amount of work still to be done, and Dr. Cox's results, in so far as he had touched on dyes used for living hair, were exceedingly welcome. During the past few years a large number of materials for dyeing hair (about which various claims were made and of which absolutely nothing was known) had been placed on the market. The position was extremely unsatisfactory. If one wanted to colour a textile or food one could order a dye under the Colour Index number, but if one wanted to dye hair one had to order the dye under some fancy name and hope for the best. He was glad that Dr. Cox had emphasised the fact that so-called henna was usually a mixture. There was a large amount of misunderstanding about this; the hairdressers still did not know what they were getting, although for years the chemist had been trying to tell them. He expressed the hope that Dr. Cox would continue his work on the dermatological effect of dyes, particularly dyes used for hair.

Dr. Cox replied that, in his experience, dyes used on human hair sometimes produced strange effects. He agreed with Mr. Redgrove that the subject was much in need of scientific study. Permanent waving, too, was apt to modify the colour of dyed hair, and he had seen some odd results due, apparently, to chemical reactions induced by, or during, permanent waving.

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The Determination of Iodine in Iodised Salt

By R. L. ANDREW, F.I.C., and J. L. MANDENO, M.Sc.

As a result of the campaign against endemic goitre, iodised salt is widely used in New Zealand. The Regulations under the Sale of Food and Drugs Act require that it shall contain not less than 1, or more than 2 parts of potassium iodide or sodium iodide in 250,000 parts. As it is important that these limits shall be observed, iodised salt is frequently examined in the Dominion Laboratory for its iodide-content.

The analytical process employed is based on that of Winkler, in which the iodide is converted to iodate by chlorine, thus, $KI + 3Cl_2 + 3H_2O \equiv KIO_3 + 6HCl$. After the excess of chlorine has been removed by boiling, potassium iodide is added, when $5KI + KIO_3 + 6HCl \equiv 6KCl + 3I_2 + 3H_2O$. The liberated iodine is titrated with standard thiosulphate solution. With certain refinements, quantities of iodine as small as $0{\cdot}2\mu$ can be determined by this method, which is therefore employed in the examination of biological materials. In iodised salt the quantity of iodine to be determined is very much larger than this.

The details of the method, as recommended by von Fellenberg, are as follows:—The salt (100 g.) is dissolved in water, the solution is made up to 500 ml. and filtered, 200 ml. of the filtrate (= 40 g. of salt) are placed in an Erlenmeyer flask, and 1 ml. of chlorine water and 2 ml. of *N* hydrochloric acid are added, together with a small piece of calcite or a few fragments of pumice, to prevent bumping. The solution is boiled until salt begins to separate. Sufficient water to dissolve the separated salt is then added, and the solution is cooled. Two ml. of strong phosphoric acid are then added, followed by about 0·2 g. of potassium iodide and a few drops of dilute starch solution, and the liquid is titrated with *N*/500 thiosulphate solution.

It was found more convenient to use bromine water instead of chlorine water, and *N*/500 thiosulphate solution instead of the stronger solution. This method, as outlined, did not give quantitative results, and the proportions of iodide in samples were calculated from the results obtained under the same conditions with solutions of salt containing known amounts of added potassium iodide. On several occasions the results were anomalous, and investigation showed that increase in the acidity of the solution lessens the amount of iodide converted into iodate. If, however, water is used instead of salt solution, the conversion is practically complete over the same range of acidity. This is shown below. In series A, 0·3 mg. of potassium iodide was added to each of 8 lots of 200 ml. of salt solution. The solutions were just alkaline to methyl orange, one drop of *N* hydrochloric acid being sufficient to render them distinctly acid. Varying amounts of acid were added. In series B, 200 ml. of water were substituted for salt solution. The experiments were then carried through, as outlined above, with the following results:

	N hydrochloric acid added ml.	*N*/500 thiosulphate required A ml.	*N*/500 thiosulphate required B ml.
1	None (just alkaline)	5·3	5·2
2	0·05	5·3	5·2
3	0·5	4·8	5·2
4	1·0	4·3	5·2
5	2·0	2·8	5·2
6	4·0	1·6	5·2
7	10·0	0·6	5·2
8	20·0	0·4	5·2

If a complete conversion took place, 5·4 ml. of *N*/500 thiosulphate solution would be required for the titration. It will be seen that in B, when water was used, almost quantitative results were obtained over the whole range, but that with the salt solution there was a distinct falling off with as little as 0·5 ml. of *N* hydrochloric acid, and with 2·0 ml. (the amount recommended by von Fellenberg) the result obtained was little more than half the theoretical. It, therefore, appears possible that the method was originally worked out by using water instead of a salt solution. In the numerous references in the literature stress is not laid upon the importance of working near the neutral point; some say, make faintly acid, some just acid, and others distinctly acid. It was found that there was no advantage in adding phosphoric, instead of hydrochloric, acid to the solution before titration. Finally, the method was modified by making the salt solution just acid to methyl orange before adding the bromine water, and adding 2 ml. of *N* hydrochloric acid before titrating with *N*/500 thiosulphate solution. Numerous experiments with salt solutions containing a wide range of known added amounts of potassium iodide have shown that the process so modified is practically quantitative over any range of values likely to be met with in practice.

The apparent loss of iodine when the process is carried out in increasingly acid solutions is of some interest. If the reaction $KI + 3Br_2 + 3H_2O = KIO_3 + 6HBr$ is the only one proceeding, and is reversible in acid solution of sodium chloride, the whole of the iodide will be present at the end of the reaction as a mixture of iodide and iodate, the proportion of each depending on the acidity of the solution. To test this, a series of experiments was carried out as in series A, down to the separation of salt; the solutions were cooled, diluted to the original volume, neutralised with *N* sodium hydroxide solution, and made just acid to methyl orange, bromine water was added, and the experiments were carried through to titration with *N*/500 thiosulphate solution. The results obtained are given under C.

N hydrochloric acid added ml.	*N*/500 thiosulphate solution required C ml.	A (for comparison) ml.
0·05	5·3	5·3
0·50	5·3	4·8
1·0	5·2	4·3
2·0	4·8	2·8
5·0	4·4	1·6
10·0	3·8	0·6
20·0	2·8	0·4

It was shown (see above under A) that near the neutral point the conversion of iodide into iodate is quantitative. If no iodine were lost from the solutions with increasing acidity, all the quantities under C would therefore be 5·3 ml. of *N*/500 thiosulphate solution. It will be seen that, with 20·0 ml. of added *N* hydrochloric acid, iodide equivalent to 2·5 ml. of *N*/500 thiosulphate has been lost from the solution, while the equivalent of 2·4 ml. has undergone reversion from iodate to iodide. In other words, with increasing acidity the conversion of iodide into iodate in presence of sodium chloride is progressively less complete, and at the same time increasing amounts of iodine (possibly as monochloride) are lost from the solution.

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A Contribution to the Iodimetric Titration of Tin

BY F. L. OKELL, F.I.C., AND JOHN LUMSDEN, B.SC., A.I.C.

(*Read at the Meeting, October* 2, 1935)

IN the iodimetric titration of tin a hydrochloric acid solution of the metal is first reduced to the stannous condition. A number of reducing agents have been recommended for this purpose; metals such as iron, aluminium, nickel, zinc and lead have generally been used; more recently, hypophosphorous acid has been advocated.[1]

The stannous chloride so obtained is titrated against a solution of iodine in aqueous potassium iodide solution, precautions being taken to prevent oxidation by air during the titration.

The reaction is given by the equation:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI,$$
$$\text{or } Sn^{++} + I_2 = Sn^{++++} + 2I^-.$$

The first method for attaining accuracy was suggested by Lenssen,[2] who carried out the titration in an alkaline tartrate solution and reported good results by iodine titration. Benas[3] found that inaccurate results were obtained in both acid and neutral solutions. He showed that the low results were due to the action of oxygen from the air, and that it was necessary to exclude air from the solution during titration, and proposed the addition of excess of iodine to the acid solution of stannous chloride, followed by titration back with thiosulphate. Young[4] obtained good results in acid solution, but his method of standardising the iodine solution against potassium dichromate by titration of stannous chloride against both these oxidising agents consists, in effect, in standardising the iodine against stannous chloride, so that his results do not prove that he had eliminated the oxygen effect. Borgman[5] found that the reaction between stannous chloride and oxygen is catalysed by potassium iodide; he, therefore, suggested the use of an alcoholic iodine solution, with cacothelin, instead of starch, as indicator. Kolthoff[6] found that Borgman's method gave results which were still somewhat too low. He noticed that the presence of a small quantity of antimony decreased the oxidation by air, and proposed its addition as an anti-catalyst; but, as the stannous chloride and oxygen reaction was not entirely suppressed in a direct iodine titration, he finished the determination by addition of excess of iodine, followed by titration against thiosulphate. Köhler[7] added to the stannous chloride solution excess of iodine dissolved in potassium thiocyanate, and then titrated back with thiosulphate. Jilek[8] obtained correct tin titrations by keeping the solution strongly acid, adding excess of iodine and titrating back with thiosulphate. Höltje,[9] for the determination of about 1 mg. of tin, added excess of dilute iodine solution containing only two to three g. of potassium iodide per l., and titrated the excess with thiosulphate.

The investigators so far mentioned used various metals to reduce the tin to the stannous condition. Evans (*loc. cit.*)[1] proposed the use of sodium hypophosphite for this purpose. Before titrating, citric acid was added, and the solution was diluted to reduce the acidity. The titration was performed in a special apparatus to secure complete exclusion of air. With pure tin solutions stoichiometric results were obtained.

Even if rigidly excluded from the stannous chloride, air is dissolved in appreciable amount in the iodine solution. This source of error has not been mentioned by any of the above workers except Köhler, who drew attention to it in the titration of tin by potassium dichromate. He expressed the opinion that in practice it is difficult to prepare and preserve air-free standard solutions.

Ramsay and Blann,[10] recognising that oxygen dissolved in the iodine solution exerted a considerable effect on tin titrations, circumvented the interference by using potassium iodate instead of iodine. The small amount of iodide produced by reduction of the iodate is not sufficient to catalyse the reaction between stannous chloride and oxygen, if the acid concentration is kept fairly low.

The position may be summarised by saying that the reaction between stannous chloride and oxygen is catalysed by both hydrochloric acid and potassium iodide; or, more correctly, by hydrogen ion and by iodide ion.

The measures which have been proposed to prevent the interference of oxygen with a tin titration may be classified under the following headings:

(i) Reducing the acid concentration; (ii) reducing the iodide concentration; (iii) adding a negative catalyst; (iv) completely preventing atmospheric air from entering the titration flask; (v) adding excess of iodine and back-titrating.

The various methods recommended for tin titrations consist essentially of combinations embodying two or more of the above precautions. Köhler (*loc. cit.*)[7] considered the preparation of an air-free standard iodine solution to be, in practice, a matter of difficulty. It would appear that most workers have overlooked the fact that the amount of oxygen present in the iodine solution is sufficient to affect a titration; or, if not, have considered that no error is introduced when the iodine solution is standardised against tin.

With regard to the above points, it may be shown that:

1. The preparation of air-free iodine solution is attended by no great experimental difficulty.
2. The air dissolved in $N/10$ iodine solution can account for an error of about 1 per cent., in $N/100$ solution for an error of about 10 per cent.
3. The oxygen does not react to the same extent in pure tin solution and in solutions containing other chlorides.

The extent and variability of the error that can be caused by the oxygen dissolved in the iodine solution are illustrated by the following figures. Tin (0·1 g.) was titrated with iodine solution of various strengths, but in all cases $N/5$ with respect to potassium iodide.

TABLE I

Strength of iodine solution	Titrations: Theoretical: From wt. of I_2 ml.	Titrations: Theoretical: Calc. from As_2O_3 ml.	Titrations: Actual ml.	Error low: ml.	Error low: Per Cent.
$N/5$	8·42	8·42	8·41	0·01	0·1
$N/10$	16·85	—	16·81	0·04	0·2
$N/20$	33·70	—	33·28	0·42	1·3
$N/40$	67·40	67·40	65·04	2·36	3·6

These results supply an explanation of the well-known objection of tin assayers to working with dilute iodine solutions.

The following table shows the results obtained with two $N/100$ iodine solutions made up (*a*) with ordinary distilled water, and (*b*) with air-free water. Both solutions were $N/5$ with respect to potassium iodide.

TABLE II

Tin taken g.	Tin found: (*a*) Ordinary iodine solution g.	Tin found: (*b*) Air-free iodine solution g.
0·0119	0·0108	0·0118
		0·0118
		0·0119

The results in Table II clearly demonstrate the large error introduced by the presence of dissolved oxygen in the iodine solution. It is this error that causes low results in tin assays when the iodine is standardised against arsenious oxide or by some other method that gives a stoichiometric result. The relative error thus produced is greater the more dilute the iodine solution.

If dissolved oxygen reacted quantitatively with stannous chloride, it would correspond with a definite increase in the oxidising power of the standard solution. Correct and consistent results should, therefore, be obtained, even in dilute solutions, provided tin was used for standardising the iodine. We find, however, that, despite such ideal conditions, the results are erratic.

The reaction is also influenced by other constituents of the assay solution. The positive catalytic effect of potassium iodide, and the negative catalytic effect of antimony chloride, have already been pointed out. When dealing with pure tin solutions, the effect of the dissolved oxygen can, it is true, be kept fairly constant by performing all titrations under the same conditions. When, however, the titration takes place in the assay solution prepared from a tin ore, the position is further complicated.

The element mainly responsible for this variation of the oxygen effect is titanium, a metal commonly associated with tin minerals. Under the conditions of a tin assay it is present in the assay solution as titanous chloride. Titanous salts are strong reducing agents, but the speed of reaction of an acid solution of titanous chloride with a solution of iodine in potassium iodide is too slow to affect a titration (Yost and Zabaro[11]).

It has been found, however, that the presence of titanium causes an appreciable increase in a tin assay. This effect is not proportional to the amount of titanium present, and has hitherto remained unexplained.

In Table III are shown the results obtained when titanous chloride is added to a tin assay. The iodine solution, of approximately $N/100$ strength and $N/5$ with respect to potassium iodide, was prepared from the laboratory supply of distilled water. It was standardised against tin and its strength found to be 0·01055 N.

TABLE III

Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Standard iodine solution ml.	Tin found g.	Error high Per Cent.
0·0119	Nil	18·95	0·0119	—
,,	0·5	19·10	0·0120	0·8
,,	1·0	19·38	0·0122	2·5
,,	2·0	19·40	0·0122	2·5
,,	5·0	19·87	0·0124	5·0
,,	10·0	19·97	0·0125	5·0

It will be noticed that the increase of titanous chloride from 5 ml. of $N/50$ solution to double that amount produced no additional increase in the amount of iodine used.

Table IV shows the effect of the addition of 5 ml. of $N/50$ titanous chloride solution to 10 ml. of $N/50$ stannous chloride solution. Both were titrated with

N/100 iodine solution, but two different solutions, similarly prepared, were employed.

TABLE IV

N/100 Ordinary iodine solution, standardised against tin

Iodine solution	Tin taken g.	Titanium added, *N*/50 $TiCl_3$ ml.	Titration, *N*/100 iodine ml.	Tin found g.
A	0·0119	Nil	18·95	0·0119
	,,	5·0	19·87	0·0125
B	,,	Nil	18·60	0·0119
	,,	5·0	20·24	0·0129

This shows that different values were obtained for the titanium effect when two iodine solutions, similarly prepared, were used. In view of this difference, it is not surprising that different assayers have disagreed about the magnitude of the titanium effect.

In Tables III and IV the iodine solution was standardised against tin. In Table V are shown the results obtained when the iodine solutions were standardised against arsenious oxide.

TABLE V

N/100 Ordinary iodine solution, standardised against As_2O_3

Iodine solution	Tin taken g.	Titanium added, *N*/50 $TiCl_3$ ml.	Titration, *N*/100 iodine ml.	Tin found g.
A	0·0119	Nil	18·95	0·0112
	,,	5·0	19·87	0·0118
B	,,	Nil	18·60	0·0108
	,,	5·0	20·24	0·0118

These results show that, if the true iodine strength of the solution is taken as standard, instead of the empirical standardisation against tin, low results are obtained when tin is titrated. The addition of titanium raises the titration to the stoichiometric figure. Paradoxical as it may sound to assayers, who have been accustomed to regard titanium as an undesirable impurity in tin assays, it is possible to obtain correct results by using the true iodine value of the solution and adding titanous chloride to the assay solution. Titanous chloride, like antimony chloride, is apparently a negative catalyst for the reaction between stannous chloride and oxygen.

It will be noticed that the amount of the titanium effect is different with the two iodine solutions; but that when arsenious oxide is used to standardise the iodine solution, the discrepancy is due to a variable error in the titration when titanium is absent. In presence of titanium, consistent results are shown by both solutions. The difference is evidently due to a difference in the amount of oxygen dissolved in the two iodine solutions.

When an air-free iodine solution is used, the addition of titanium produces no effect on a tin assay.

Results obtained with air-free *N*/100 iodine are shown in Table VI.

TABLE VI

Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Tin found g.
0·0119	Nil	0·0118
		0·0118
	5·0	0·0119
		0·0119
		0·0120
0·0237	Nil	0·0238
		0·0239
	5·0	0·0238
		0·0239
		0·0239

It has been shown by Tomiček[12] that cuprous chloride catalyses the reaction between titanous chloride and iodine. It might, therefore, be expected that the presence of copper in a tin assay would cause a high result when titanium is also present. The figures in Table VII shows that, with small amounts of copper, this effect is not apparent.

TABLE VII

Tin taken g.	Titanium added, $N/50$ $TiCl_3$ ml.	Copper added g.	Tin found g.
0·0237	5·0	Nil	0·0239
		0·0001	0·0238
		0·0004	0·0239
		0·0008	0·0239
		0·0008	0·0240
		0·0010	0·0239

If all the titanous chloride reacted with iodine it would correspond to an increase of the tin found by 0·0059 g. We have not further studied the effect of copper.

PREPARATION OF AIR-FREE IODINE SOLUTION.—About 1100 ml. of distilled water were boiled in a flask, A, Fig. 1, in presence of a gentle current of carbon dioxide from a suitable generator, for about an hour. The clip (*a*) was then closed, and the flask cooled to a few degrees below laboratory temperature while still connected with the supply of gas. The flask was shaken occasionally until the water was saturated with gas, as shown by no alteration in the acid level of the generator on further shaking.

The necessary quantity of potassium iodide was placed in the graduated litre flask, Fig. 2, B, provided with an extra mark to allow for the volume of the weighing bottle carrying the iodine. The flask was then cleared of air by displacement with carbon dioxide, through a tube (*b*) reaching nearly to the bottom. The weighing bottle, carrying the iodine, was then dropped in, and the gas leading tube (*b*) was changed for a shorter, drawn-out tube (*c*), connected with the long tube (*d*) of the air-free water flask, A, by means of a length of black rubber tube carrying a pinch-cock (*e*). The rubber tube had been previously filled with water by raising the pressure on the gas generator, by means of a rubber-bulb connected with the acid side of the generator. The transference was made against a current of carbon dioxide led in through (*f*). For the sake of avoiding repetition we may here explain that all operations involving the breaking of a joint or transference of liquid were made against a counter-current of carbon dioxide or the back pressure from a second generator.

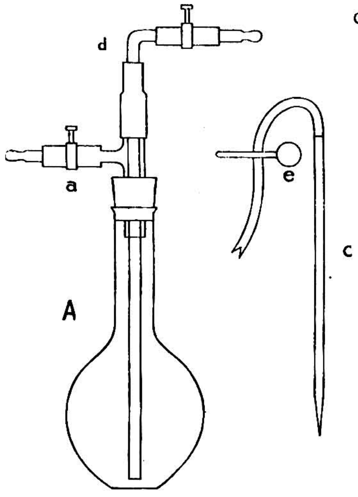

Fig. 1.

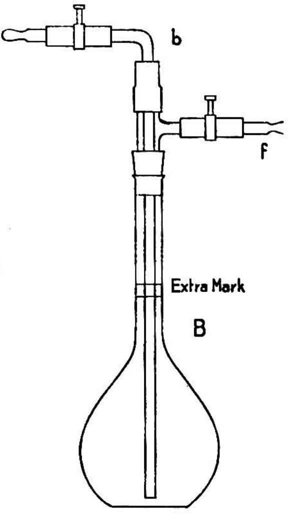

Fig. 2.

A little water was first run in to supply concentrated potassium iodide for solution of the iodine; this effected, the bulk was made up to the mark, shaken and transferred to the stock-bottle of a self-filling burette, arranged for the preservation of the solution under carbon dioxide, the stock-bottle and burette being first cleared of air by the same method.

No trouble was experienced from contact of iodine with rubber connections, provided that red rubber pressure-tube was used. Black, lightly vulcanised tube was unsatisfactory. Red rubber is not entirely free from attack by iodine, but was found soon to reach a condition in which no further action could be detected.

The carbon dioxide was prepared from marble and hydrochloric acid.

METHOD FOR REDUCTION OF TIN SOLUTIONS PREVIOUS TO TITRATION.—To the solution of tin chloride, contained in a 300-ml. round, flat-bottomed flask were added 20 ml. of concentrated hydrochloric acid (1·16 sp.gr.), 25 ml. of water, and 1 g. of aluminium turnings. After about an hour, when the action of the acid on the aluminium had almost ceased, 20 ml. of concentrated hydrochloric acid were added, a cork carrying an eduction tube was fitted, and the contents of the flask were heated to boiling. When the remaining aluminium and the precipitated tin had dissolved, the eduction tube was connected with a supply of carbon dioxide while steam was still issuing (Beringer, *Text-book of Assaying*, 1908), and the flask was cooled in a bath of cold water. When cold, the solution was immediately titrated without further special precautions.

Tin solutions cooled and titrated under the above conditions gave stoichiometric results with air-free iodine solutions, standardised against arsenious oxide; proving that the stannous chloride was completely reduced and suffered no oxidation by air during cooling or titration (*cf.* Table VI).

SUMMARY.—We have shown that low results in tin titrations are due, not to incomplete exclusion of gaseous oxygen from the titration flask, but to oxygen dissolved in the iodine solution.

The various methods that have been advocated for the improvement of tin titrations are, in effect, methods of preventing the reaction of dissolved oxygen. This has not always been the avowed object of the investigators. For instance, Ibbotson and Brearley[13] used antimony as a reducing agent; the antimony chloride formed was subsequently shown by Kolthoff[6] to be a negative catalyst for the oxygen reaction. From their paper, however, it is clear that they had quite different ideas as to why the antimony reduction gave good tin titrations.

It will probably be generally agreed that:

1. A stoichiometric titration for the determination of an element is preferable to one in which there occurs a constant error, neutralised by standardising the volumetric solution under the same conditions as for assays.
2. A direct titration is preferable to a determination made by addition of excess of a reagent, followed by back-titration.
3. The standard solution should contain no impurity that interferes with a titration; in this instance, oxygen.

The above considerations lead to the conclusion that the best method of titrating stannous chloride is by means of an air-free solution of iodine.

The general argument, so far as tin is concerned, is re-inforced by the following specific consideration:

The assumption that the oxygen interference is a constant effect, which can be neutralised by standardisation of the iodine solution against tin, is not justified in the assaying of tin ores. Titanium is the main cause of inconstancy of the oxygen effect; and this is the only interference that titanium, by itself, exerts on tin assays. The removal of titanium from a tin ore involves a troublesome separation, which is unnecessary when an air-free iodine solution is used for titration.

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DISCUSSION

Dr. J. J. FOX said that many years ago Dr. Farmer had described how to obtain air-free water by bubbling carbon dioxide through it.

Dr. B. S. EVANS said that he regarded the paper as a valuable contribution to the literature of the subject. There were, however, certain points that were not clear to him. He understood that starch was the indicator used; his own experience of starch was, first that it required an appreciable amount of iodine to produce the colour; and, secondly, that its sensitiveness varied enormously with the proportion of potassium iodide present; if the potassium iodide-content were reduced, the end-point might be affected. The question of air in the iodine solution had not occurred to him, and he would not have thought that it could exert such an influence. As regards the effect of other elements, he thought that it was generally desirable to make a preliminary separation of the tin; the presence of copper, at any rate, was fatal to accuracy. He assumed that the antimony mentioned was the chloride and not the metal, for it had been shown conclusively that metallic antimony would interfere with the titration. With regard to the reduction with aluminium, he, personally, regarded all reductions of tin with metals as suspect. He understood that his own figures obtained with hypophosphite reduction were not challenged.

THE AUTHORS (in a written reply) say: The indicator was prepared from potato starch, which had been rendered soluble by treatment with 2 per cent. v.v. hydrochloric acid. The sensitiveness of the starch-iodide end-point was influenced by the concentration of potassium iodide. All their iodine solutions were $M/5$ with respect to potassium iodide. This provided sufficient for a sharp end-point in the assay solution, with the smallest quantity of standard solution used in a titration. "Blanks," with the same quantity of potassium iodide added, gave an end-point with one drop of $N/100$ iodine solution.

The antimony mentioned in connection with its catalytic action was in the form of chloride. The figures obtained by Dr. Evans by means of hypophosphite reduction were not questioned in any way. The object of the paper was to show that the direct titration of stannous chloride by iodine could be affected by an error which had been generally overlooked, namely, the presence of air in the standard solution. Dr. Evans's work was carried out under conditions very different from theirs, and they had made no study of them; but, in view of their results, it seemed probable that his stoichiometric figures were due to the high dilution employed, the low concentration of acid and potassium iodide; or, possibly, to the fact that hypophosphorous acid acted as an anti-catalyst in the oxygen and stannous chloride reaction.

With regard to metallic reducers, their figures showed that reduction with aluminium was complete. In this connection the possibility of attributing a low result, caused by air in the standard solution, to incomplete reduction by a metal, should not be overlooked.

31 CANNON'S DRIVE
EDGWARE, MIDDLESEX

The Determination of Magnesium in Duralumin

By G. STANLEY SMITH, B.Sc., A.I.C.

In the analysis of aluminium alloys the determination of magnesium often causes much trouble. It is usually estimated in the residue left after a caustic soda attack, elements interfering in the phosphate precipitation being removed by the group reagents or held in solution by the addition of tartaric acid. Re-precipitations, with the consequent accumulation of ammonium salts in the solution are necessary if aluminium, iron and manganese are removed by means of bromine and ammonia or of ammonia and ammonium sulphide, and it is by no means easy to get rid of all the manganese. The magnesium ammonium phosphate must in any case be precipitated twice and the ignited pyrophosphate examined for manganese.

The method to be described eliminates reprecipitations and is rapid and simple, and the results are trustworthy. The removal of aluminium, iron and manganese from a dilute sulphuric acid extraction of the caustic soda residue is accomplished by means of zinc oxide and potassium permanganate, as in a Volhard titration, but without the need for obtaining an exact end-point, the excess of permanganate being removed by alcohol. Magnesium hydroxide is then thrown down in the filtrate by means of sodium hydroxide and potassium cyanide, the latter serving to keep in solution any copper or nickel. The precipitate is dissolved in dilute acid, and the magnesium is determined as pyrophosphate or, less accurately, by adding excess of $N/10$ sodium hydroxide solution to the neutral solution and titrating the excess in a portion of the clear solution.

Since the magnesium ammonium phosphate is precipitated in an almost pure solution of magnesium sulphate, a reprecipitation is unnecessary. The time required for a determination, including a standing period of 4 hours for the precipitation, is about 7 or 8 hours. If the volumetric method is used, the time can be reduced to about 2 hours.

METHOD.—Dissolve 2 g. of the alloy in 60 to 70 ml. of sodium hydroxide solution (10 per cent.). Filter through a 9-cm. Whatman, No. 40, filter-paper, and wash thoroughly with hot water. Hold the funnel in a horizontal position and, without removing the paper, wash back the insoluble residue into the original beaker with hot water. Add 5 ml. of dilute sulphuric acid (sp.gr. 1·2), boil for about a minute, pour the solution through the paper, and wash the residue of copper with hot water. The residue contains no magnesium, but a little copper is certain to go into solution. To the filtrate add sodium hydroxide solution until a slight precipitate forms. Clear the solution with a drop of dilute sulphuric acid and run in from a burette $N/10$ or $N/20$ permanganate to oxidise the iron. Boil the solution and add zinc oxide emulsion in slight excess. Continue the addition of permanganate to the nearly boiling solution until the liquid is coloured pink and remains pink on further boiling and on the addition of a little more zinc oxide. Then add 2 or 3 drops of alcohol and boil again for a few minutes to remove the permanganate. Filter the solution and wash with hot water. The filtrate is free from aluminium, iron and manganese, but contains a little copper not precipitated by zinc oxide, and also nickel, if present in the alloy. Add about 1 g. of potassium cyanide and 10 ml. of 10 per cent. sodium hydroxide solution, boil for 2 or 3 minutes, introduce about half a 9-cm. filter-paper as pulp, mix well, filter after standing a short time, using a 9-cm. paper, and wash several times with 1 per cent. sodium hydroxide solution. The solubility of magnesium hydroxide is negligible in the presence of alkali. Transfer pulp and precipitate to the beaker without removing the filter-paper, add rather more dilute sulphuric acid than is needed to give an acid reaction to methyl orange, stir well to make sure that the magnesium hydroxide has dissolved, pour through the same filter-paper, and wash with hot water. Add a little ammonium chloride and then ammonia to make the solution slightly alkaline. The absence of a precipitate confirms the completeness of the separation of aluminium and iron by zinc oxide. Make slightly acid, add a small quantity of microcosmic salt or ammonium phosphate, boil and add an excess of ammonia. Leave the solution for about 4 hours, filter through a No. 40 paper, wash with 2 per cent. ammonia, ignite and weigh the magnesium pyrophosphate.

Instead of the magnesium being precipitated as phosphate it may be determined speedily by titration, the results being sufficiently accurate for most purposes. After dissolving the hydroxide in sulphuric acid add dilute sodium hydroxide solution till the reaction is alkaline, make acid with $N/10$ sulphuric acid, boil to remove any carbon dioxide, cool and make the solution exactly neutral by means of $N/10$ acid and alkali, using a reference solution to obtain the correct tint of methyl orange. Transfer to a 250-ml. volumetric flask, run in 50 ml. of $N/10$ sodium hydroxide solution, fill to the mark, and mix. After about 10 minutes filter off 200 ml. and titrate the excess of alkali with acid (1 ml. $N/10$ NaOH $\equiv$ 0·001216 g. Mg.).

The method has been tested on a large number of dural samples, in which the magnesium-contents varied from 0·35 to 0·80 per cent. The results obtained by the gravimetric method agreed to the second decimal place with those obtained by other satisfactory methods. By the volumetric method slightly higher results were usually given, to the extent of 2 or, at most, 3 units in the second place. These are explained by the impossibility of separating zinc completely from magnesium by a single treatment with sodium hydroxide and cyanide; also, by the difficulty of obtaining the exact end-point in the titration. Methods of titrating solutions of magnesium salts are discussed by Kolthoff.[1]

Results obtained by the gravimetric method with a solution of the sulphates of the various metals are shown in the table below. In precipitating magnesium

Elements present (weight in g.):

	Al	Fe	Mn	Cu	Ni	Mg	Mg. found
(i)	—	—	—	—	—	0·0255	0·0255
(ii)	0·01	0·02	0·025	0·01	—	0·0255	0·0256
(iii)	0·10	0·02	0·025	0·01	0·01	0·0255	0·0255
(iv)	0·05	0·04	0·05	0·02	0·02	0·0255	0·0256
(v)	0·01	0·02	0·025	0·01	—	0·0510	0·0511
(vi)	0·25	0·04	0·05	0·02	0·02	0·0010	0·0014

hydroxide with sodium hydroxide the reagent was added in quantity sufficient to redissolve the zinc hydroxide.

In (vi) the pyrophosphate contained a little zinc, but none of the magnesium had been lost.

The magnesium pyrophosphate precipitate has been repeatedly tested for manganese, but in no instance has more than the equivalent of 1 drop of $N/20$ potassium permanganate solution been found—an amount which may be regarded as negligible. According to Sarkar and Dhar[2] a compound 2MgO, $7MnO_2$, xH_2O (where $x = 19$ or 13) is formed by the interaction of permanganate with a solution of a manganese salt containing magnesium. The formation of such a compound would obviously invalidate the method described. In no instance, however, has the manganese precipitate, produced in the presence of a slight excess of zinc oxide, contained more than a trace of magnesium.

REFERENCES

1. I. M. Kolthoff, *Volumetric Analysis*, Vol. II, 1929.
2. P. B. Sarkar and N. R. Dhar, *Z. anorg. Chem.*, 1922, **121**, 135.

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Notes

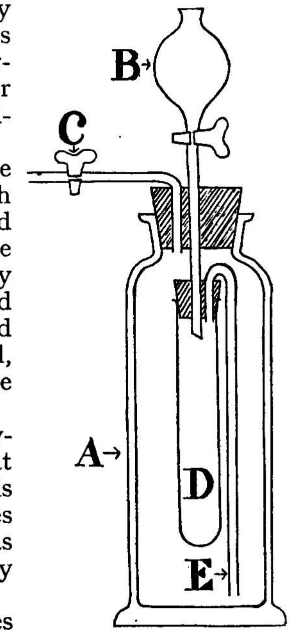
The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

METHOD FOR DETERMINING "AVAILABLE" AND "TOTAL" CARBON DIOXIDE IN BAKING POWDERS AND SELF-RAISING FLOURS

THE published methods for these determinations are, in the main, lengthy, or require special apparatus, or are not very accurate. The method now to be described is essentially a modification of that given by Hepburn (ANALYST, 1926, **51**, 622), and the interpretation of "available" carbon dioxide is that suggested by Liverseege (*Adulteration and Analysis of Food and Drugs*, p. 435).

APPARATUS.—The apparatus consists of a tall thick-walled glass vessel, A (an absorption tower of 400 ml. capacity is suitable), fitted with a tap funnel, B, and a glass tap, C. The funnel stem runs directly into a stout glass boiling tube, D (about 50 ml. capacity), from which a delivery tube, E, leads almost to the bottom of A.

METHOD.—A suitable quantity of the sample (0·2 to 0·3 g. of baking powder or about 3 g. of self-raising flour) is weighed into the tube, D, 50 ml. of $N/10$ barium hydroxide solution and about 50 ml. of carbon dioxide-free water (to increase the column of absorbing liquid) are placed in A, and the apparatus is assembled as shown in the diagram, and then evacuated for about 10 minutes. (It is essential that the apparatus should be air-tight, otherwise the liquid in A may be forced back into D.) The glass tap, C, is then closed, and 20 ml. of water (for "available" carbon dioxide) or 20 ml. normal hydrochloric acid (for "total" carbon dioxide) are run in very gradually from the tap funnel while the apparatus is gently shaken. The liberated carbon dioxide is mainly absorbed by the baryta as the gas bubbles through it. The absorption is allowed to proceed with occasional shaking, to prevent surface saturation and to quicken absorption, for 3½ to 4 hours, a period which we have found to be adequate. At the end of this time the vacuum is destroyed by gradually opening the tap of the funnel, the rubber bung and attached tubes are removed, their surfaces being rinsed into A with a little water, and the residual baryta is titrated with *N*/10 oxalic acid, phenol-thymolphthalein being used as indicator.* A point to note, and one not very generally known, is that this indicator (*p*H 8·3 to 11·0) is most satisfactory for acid-alkali titrations where interference of carbonates is to be avoided; the end-point is distinct and the colour-change sharp, from deep blue to colourless. In our experience phenolphthalein gave a very indefinite end-point owing to repeated fading.



"Total" carbon dioxide can be determined on the same quantity of the sample by pipetting a fresh quantity (50 ml.) of *N*/10 baryta into the bottle, A, and replacing the tube in position. After evacuation of the apparatus as before, 20 ml. of normal acid are run in very cautiously and the liberated carbon dioxide is determined as before. The difference between the "available" and "total" carbon dioxide in most cases is, however, small, and therefore we make a practice of determining the latter on a fresh quantity of the sample.

In Table I are recorded results obtained with freshly-ignited sodium carbonate, A.R. It will be seen that between 96 and 99 per cent. of the carbon dioxide is absorbed in 2 hours, and that total absorption takes place in 3½ to 4 hours. No appreciable difference was observed in the time for complete absorption by doubling the quantity of baryta (Experiment 6).

Baking Powders.—In connection with these analyses (Table II) we examined some tartrate and some phosphatic powders to make certain that 4 hours were adequate for the latter, as they liberate their carbon dioxide rather slowly.

Self-raising Flours.—Since the sale of this article was legalised by the Bread Acts Amendment Act, 1922, its use has steadily increased, but no attempt has yet been made to fix any standard for the "available" carbon dioxide on which the value of such an article depends. No such attempt was made in the Agricultural Produce (Grading and Marking) (Wheat Flour) Regulations, 1933, which requires that self-raising flour "shall contain such ingredients or mixture of ingredients in such quantities and proportions as are properly required to make the flour self-raising."

In the determination of "available" carbon dioxide in self-raising flour, water should be added very cautiously to avoid frothing over. The use of alcohol (*cf.* Callan, ANALYST, 1927, **52**, 222) to prevent frothing was not found satisfactory.

SUMMARY.—1. A simple method is described for the determination of "available" and "total" carbon dioxide, requiring no special apparatus and little manipulation, applicable to a small quantity of sample and sufficiently accurate to give results agreeing to within 0·1 per cent. of the theoretical.

2. The apparatus devised, being entirely rigid and without loose parts, is easy to handle, and as the CO_2 liberated is actually made to bubble through the

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* We also tried thymolphthalein whose *p*H range (9·3 to 10·5) is somewhat similar, but the colour-change is not nearly so sharp, owing to the blue colour in alkaline solution being very faint.

baryta solution, the period for complete absorption is shortened to only 4 hours as against 12 to 24 hours in Hepburn's method.

3. The indicator phenol-thymolphthalein offers distinct advantages over phenolphthalein and thymolphthalein.

TABLE I

EXPERIMENTS WITH FRESHLY-IGNITED SODIUM CARBONATE

(Theoretical CO_2-content 41·52 per cent.)

Time of absorption Hours	Weight taken g.	$N/10$ baryta used ml.	Carbon dioxide found Per Cent.
16	0·111	20·95	41·52
24	0·106	20·00	41·51
1½	0·090	16·35	39·96
2	0·098	18·35	41·19
2	0·198	36·40	40·45
2	0·101	18·60*	40·51
3	0·109	19·80	39·96
3½	0·097	18·65	41·45
4	0·099	18·65	41·45
4	0·098	18·45	41·42
4	0·100	18·85	41·48
4	0·106	20·00	41·51
4	0·197	37·10	41·43

* Double quantity (100 ml.) of baryta taken.

TABLE II

BAKING POWDER

Sample	Type of raising ingredient	"Available" CO_2 found 4 hours Per Cent.	"Available" CO_2 found 16 hours Per Cent.	"Total" CO_2 found 4 hours Per Cent.
Baking powder 1	Tartrate	9·20	9·20	9·40
,, ,, 2	,,	8·97	8·90	11·10
,, ,, 3	,,	10·31	10·39	10·90
,, ,, 4	,,	8·33	8·17	9·60
,, ,, 5	Phosphatic	3·67	3·70	4·30
,, ,, 6	,,	6·50	6·41	7·90
,, ,, 7	,,	4·49	4·60	5·60

TABLE III

SELF-RAISING FLOUR

Sample	Available carbon dioxide found 4 hours Per Cent.	Available carbon dioxide found 16 hours Per Cent.
Self-raising flour 1	0·35	0·38
,, ,, 2	0·31	0·32
,, ,, 3	0·35	0·40

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EXTRACTION OF LEAD BY MEANS OF DIPHENYLTHIOCARBAZONE

In the examination of foodstuffs and biological materials for traces of lead by wet oxidation with sulphuric and nitric acids, followed by the diphenylthiocarbazone extraction method of Allport and Skrimshire (ANALYST, 1932, **57**, 440), considerable difficulty has frequently been experienced in the colorimetric matching of the final solutions.

This trouble was encountered in the examination of organs by Roche Lynch, Slater and Osler (ANALYST, 1934, **59**, 787), and they had not been able to devise a method for its removal. The colour developed is probably due, as they suggest, to nitro bodies which are resistant to further oxidation by nitric and sulphuric acids, and are extracted by the chloroform. Possibly the interfering colour may be avoided by using other methods for oxidation of the original material, but for large bulks these prove tedious.

The following method has been developed and used with complete success for some time. The residues obtained after evaporation of the chloroform are warmed with 2 ml. of concentrated sulphuric acid on a water-bath for a few minutes to destroy the organic compound, 10 ml. of 6 per cent. hydrogen peroxide are added, and the mixture is boiled until white fumes are evolved. After addition of 2 g. of pure ammonium persulphate the flask is heated on an asbestos gauze over a Bunsen burner for half an hour. The resulting solution is colourless, and does not develop any yellow tint with ammonia. D. C. GARRATT

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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.

GIBRALTAR

REPORT OF THE CITY ANALYST AND BACTERIOLOGIST FOR THE YEAR 1934

THE total number of specimens and samples examined during the year was 4589, of which 102 were samples of food and drugs.

GOATS' MILK.—Of the 48 samples of milk taken by the sanitary inspectors, 40 were of goats' milk and 8 of cows' milk. The statutory limits for goats' milk are: Fat, 3·5; non-fatty solids, 8·0 per cent. The average composition of the samples examined was: Milk fat, 4·34; non-fatty solids, 8·83 per cent.

IMPORTED UNBOILED MILK.—No sample of imported milk was found to be wholly unboiled. Of the 28 samples examined, 4 contained 8, 4, 3, and 3 per cent. of unboiled milk, respectively. The Public Health Ordinance demands that all imported milk shall be "boiled, pasteurised or sterilised."

The Ortol Test for Unboiled Milk.—Further experimental work on the ortol test for the detection and estimation of small quantities of unboiled (raw) milk in boiled milk has been done. Varying degrees of brick-red colour are obtained according to the amount of unboiled milk present. The colour obtained with boiled milk containing from 1 to 20 per cent. of unboiled milk can readily be matched if the control admixtures (*i.e.* boiled milk plus raw milk) are made previously and are ready to receive the ortol and hydrogen peroxide at the same time as the sample under examination. The question arose whether by heating a raw unboiled milk at various possible temperatures and varying the duration of heating, the enzymes (responsible for the deep brick-red colour given by raw milk) could be partly destroyed. This would mean that only a partial red colour would be obtained and mislead the analyst to assume that a percentage of raw milk was present. Under the conditions applicable to Gibraltar, it may be necessary to give evidence on this point in court. I tried to match the depth of colour given by a boiled milk containing 8 per cent. of unboiled raw milk, and found that this was possible by heating raw milk to 73° C. for 10 minutes.

Below are given the results obtained by heating raw milk at different temperatures for varying lengths of time and quickly cooling it before adding ortol and hydrogen peroxide.

Temperature ° C.	Duration of heating Minutes	Colour obtained with ortol and hydrogen peroxide
70	30	Full, as for raw milk
72	15	Full, as for raw milk
72	30	Half, as for 50 per cent. raw milk (approx.)
73	10	Partial, as for 8 per cent. raw milk
73	20	Slight, as for 1 per cent. raw milk
73	30	None, as for boiled milk
75, 76, 77	25	None, as for boiled milk
75, 76, 77	20	Some, as for 2 per cent. raw milk
80, 82, 83	10	None, as for boiled milk
80, 82, 83	5	Slight, as for 1 per cent. raw milk
84	5	None, as for boiled milk
85	1	None, as for boiled milk

The ortol test does not show whether a milk has been pasteurised (62·8°–65·5° C. for ½ hr. and quickly cooling), and the lowest temperature with 30 minutes' heating which gave no colour with ortol was 73° C.

In making these tests 10 ml. of milk were heated in a test-tube in a water-bath. The milk was quickly cooled before adding the ortol (0·5 ml. of 5 per cent. solution) and hydrogen peroxide (1 to 5 drops of 10 vol. solution). Three minutes were allowed for colour to develop. Too much hydrogen peroxide tends to destroy the colour.

ICE CREAM.—Inspection of the ice creams sold in Gibraltar was undertaken, and four different supplies were bacteriologically examined. It is not at present practicable to lay down definite bacteriological standards, but, as a rough guide, Buchan has suggested that ice creams made under clean conditions shall

(1) not contain more than 1,000,000 organisms per ml. growing at 73° C.
(2) not contain *B. coli* in less quantity than 0·1 ml.;
(3) not contain streptococci in less quantity than 0·001 ml.;
(4) not contain *B. enteritidis sporogenes* in less than 10 ml.

The results obtained from the four samples of ice cream examined were as follows:

	No. 1	No. 2	No. 3	No. 4
Total organisms growing at 37° C. per ml.	41,610	110,400	2,110,000	4,992,000
B. coli	In 0·1 ml.	In 0·1 ml.	In 0·000001 ml.	In 0·00001 ml.
Streptococci	In 0·01 ml.	In 0·1 ml.	In 0·1 ml.	In 0·1 ml.
B. enteritidis sporogenes	Not in 30 ml.	Not in 30 ml.	Not in 30 ml.	Not in 30 ml.

Ice creams Nos. 1 and 2 were considered satisfactory, but Nos. 3 and 4 were not up to the desired bacteriological standards.

ANTHRAX IN SHAVING BRUSHES.—Samples of tooth brushes purchased from shops contained no anthrax bacilli, and were found to be sterile. Shaving brushes were also examined. One sample was found to be infected with *B. anthracis*, and the consignment was withdrawn from sale.

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CITY OF SALFORD

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1934

THICK CREAM.—A sample of tinned cream, labelled "Pure Thick Cream," contained 20 per cent. of fat. Although the average purchaser would associate (perhaps subconsciously) the word "thick" with a high fat-content, it is obvious that proceedings would be likely to fail, since the producers could say that "thick" referred to the physical condition. It is suggested that the following standards should be set up for cream (including tinned cream):

Double (or thick) cream	..	50 per cent. of butter-fat
Thin cream	..	20 ,, ,, ,,

BOOK LICE IN FLOUR.—A sample of self-raising flour was found to contain live insects which were identified at the Zoology Department, Manchester University, as the common book louse. This insect derives its name from the fact that it frequents the bindings of books, where it lives upon the starchy paste; it is not harmful. The insects probably got into the flour in the shop, and the shopkeeper was therefore advised to give the shelf and its vicinity a thorough cleansing with disinfectant.

CASTOR OIL PILLS.—A formal and an informal sample contained not more than 2 per cent. or 1/10 minim of castor oil per pill. As the medicinal dose is 60 to 480 minims, it is obviously impossible for a pill to contain even a moderate dose of the oil. Powders and pills containing the active principle of castor oil have had only a limited sale. The particular pills approximated in composition to the compound rhubarb pill of the B.P., and after an interview the manufacturers agreed to label them as "Aperient Pills"—and to add, in smaller type, "a substitute for castor oil."

LYSOL.—Four of 5 samples of lysol submitted were adulterated. They contained 2·2 to 2·8 per cent. of cresol. Two stated on the label that they contained not more than 3 per cent. of cresols, and one claimed to be "approved by Health Authorities."

In the original patent for lysol by Dammann in 1891 no strength was specified, but the only strength prepared by the patentee was 50 per cent. of cresols in a soapy solution, and when, after 1914, a number of British firms prepared lysol, this was the strength adopted by them all. If the standard in the B.P. 1932 is compared with the amounts of cresols in the samples mentioned above, it will be seen that they contain about 1 part of lysol in 20 parts of water. In the dilution recommended, namely, one tablespoonful to the pint, they would be practically useless as disinfectants.

Summonses under the Merchandise Marks Act, 1887, were issued against the retailers of three samples for selling an article to which a false trade description was applied, and against the makers for applying a false trade description. The makers and wholesalers were also summoned under the Summary Jurisdiction Act, 1848, for aiding and abetting, counselling and procuring the retailer in the sale, and convictions were obtained (*cf.* ANALYST, 1934, **59**, 693).

LYSOL SOAP.—Four samples, purchased as lysol soap, contained the following amounts of cresols:

Cresols, per cent. ..	2·8	0·25	0·6	0·8
equivalent to lysol, per cent.	5·6	0·5	1·2	1·6

Experiments were made to determine the minimum percentage of lysol in a soap which would justify its being called "Lysol" soap. The usual dilution of "Lysol" recommended for washing the hands is 1 per cent., and a 0·5 per cent. solution is stated to have a disinfectant action upon the skin. Therefore a lysol soap might reasonably be expected to be one which, in use, results in at least a 0·5 per cent. solution of lysol being applied to the skin. An estimation of the amount of lather left on the hands after rubbing with soap at 50° C., so as to form a good lather, gave the following results:

Time of lathering Seconds	Total solids in lather Per Cent.	Equivalent of soap (on basis of 30 per cent. water)
5	10·6	15
10	16·1	23

In the average use of soap the percentage of soap in the lather formed is thus not likely to exceed 25. For this lather to contain 0·5 per cent. of lysol, the soap must contain not less than 2 per cent. of lysol. On this basis it is reasonable to conclude that a reasonably good lysol soap contains not less than 4 per cent. of lysol, and that 2 per cent. is a minimum standard.

PHENOLATED IODINE SOLUTION.—A sample contained: iodine, 0·05; potassium iodide, 0·5; and phenols (as cresylic acid), 0·5 per cent. Although there is no standard for this article, it was so deficient in all its constituents that it was condemned as adulterated. A reasonable standard would be: iodine, 2·5; phenol, 2 per cent. A sample previously examined passed this standard.

H. E. MONK

CITY OF BIRMINGHAM

REPORT OF THE CITY ANALYST FOR THE SECOND QUARTER, 1935

OF the 1362 samples of foods and drugs examined, 1293 were bought informally and 69 formally.

SULPHUR DIOXIDE IN BLACKCURRANT JAM.—A sample contained 50 p.p.m. of sulphur dioxide. The firm explained that blackcurrant pulp was very tenacious of the sulphur dioxide used as a preservative, and that representations to this effect had been made to the Ministry of Health by a number of firms with a view to getting the permissible amount allowed in blackcurrant jam raised to 100 parts per million, but without success. The firm was now incorporating with the pulp a proportion of blackcurrants preserved by heat, to prevent an undue amount of sulphur dioxide appearing in the finished jam.

TIN IN SILD IN OLIVE OIL.—An informal sample contained 5·3 grains of tin per lb., and a formal sample 5·4 grains. Both tins were badly corroded. A report to the Local Government Board in 1908 by Drs. Buchanan and Schryver (*cf.* ANALYST, 1909, **34**, 121) stated that the presence in food of more than 2 grains per lb. of tin might be taken to signify that it had become potentially deleterious to health and these samples were, therefore, condemned.

Correspondence with the wholesale dealers concerned elicited the information that this was the first complaint received by them, although millions of tins had been imported by them from Norway. The tinplate used was of English manufacture. They were writing to the Norwegian suppliers in order to try and trace any possible source of the trouble.

"NON-TANNIC" TEA.—The label on the packet of a sample of tea contained the statements that it was "Non-tannic," "Free from stalk which contained crude tannin," and "Digestive because non-tannic." The amount of tannin was 16 per cent., a figure rather higher than the average. Correspondence with the firm responsible for the packing is still proceeding, but the words "Non-tannic" have already been withdrawn in the latest type of package. H. H. BAGNALL

Ministry of Health

Sale of Food and Drugs

EXTRACTS FROM THE ANNUAL REPORT FOR 1934–1935, AND ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1934*

THE total number of samples analysed by Public Analysts in England and Wales during 1934 was 140,583, and of these, 7451 (5·3 per cent.) were reported against, *i.e.* a slight decrease over those of the previous year (5·5 per cent.).

PRESERVATIVES.—Of 418 contraventions of the Public Health Regulations, the added preservative would have been permissible in 152 cases (148 of sausages) if it had been properly declared. Boron in cream, milk, ice-cream, biscuits, sausages, tripe, potted meat, wines, etc.; sulphur dioxide in cream, barley, pepper, minced, potted and other meats, and formaldehyde in milk were reported. A "tripe bleach" consisted of sodium perborate; and 2 samples of a "preservative liquid" were 4·5 and 4·7 per cent. aqueous solutions, respectively, of formaldehyde.

MILK.—Of 76,930 samples, 5506 were reported adulterated or not up to standard. Of the 1020 "appeal-to-cow" samples, 342 were below the presumptive standard of the Sale of Milk Regulations. Visible dirt was present in 8 samples, paraffin in 1, added colouring matter in 12, formaldehyde in 18, and boron preservative in 3. Twenty-two samples of graded milks were deficient in fat, and 25 skimmed milks and 1 buttermilk were reported against.

CONDENSED AND DRIED MILK.—Only 22 of 1098 samples of condensed milk were reported against, including unsound samples (one a milk containing tin in a blown tin), and 7 samples of dried milks.

CREAM.—Of 2024 samples examined, 11 contained boron preservative, 5 sulphur dioxide, 1 added colouring matter, 1 tin, and 1 sample 1·53 per cent. of lactic acid. Two samples were deficient in butter-fat, and 2 samples labelled "Pure Thick Cream" and 1 "Thick Rich Cream" were considered to be too poor in fat to justify the labels.

BUTTER AND MARGARINE.—Of butter, 73 of 8612 samples, and of margarine, 23 of 3013 samples, were reported against, mostly for containing excess of water.

LARD AND OTHER FATS.—Adverse reports on 10 samples out of 2675 were accounted for by 7 samples consisting wholly or partly of foreign fat, 1 containing 1·2 per cent. of water, and 2 containing excess of free fatty acids. Excess of rice flour or other starchy material was present in most of the 39 incorrect suet samples (of 490 examined), whilst of the 524 samples of dripping, 1 consisted wholly of vegetable fat, 1 had an excess of free fatty acids, and 8 contained excess of water.

CHEESE.—Of 1432 samples, 19 were reported against; 7, sold as cream cheeses,

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* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3d. net.

were whole-milk cheeses, and 2 samples of "double cream" cheeses had water as their principal ingredient.

BREAD AND FLOUR.—The 275 samples of bread were all satisfactory, and of 1269 samples of self-raising flour, 1 contained 1·5 p.p.m. of lead, 1 excess of mineral matter, and 1 contained book lice.

JAM AND MARMALADE.—Excess preservative accounted for the adverse reports on 32 samples of 1486 examined, and the remaining 62 samples were mostly deficient in fruit or soluble solids.

VINEGAR.—Of 1716 samples, 173 were adulterated or below standard, which is a considerable increase over those of 1933 (98 of 1746). Deficiency in acetic acid accounted for 110 samples, and 7 samples contained vinegar eelworms, and 1 sample contained copper.

SPIRITS AND BEER.—Of 1841 samples, 72 of whisky, 25 of gin, 22 of rum, and 4 of brandy had had the spirit reduced below 35° U.P. Six beers contained excess of preservative, 5 contained excess of lead, and 1 had 0·3 per cent. of carbolic disinfectant, in a total of 496 samples.

MISCELLANEOUS ARTICLES OF FOOD.—Over 30,000 samples of other foods of very varied descriptions were examined. Nine samples sold as coffee contained chicory, 1 to the extent of 62 per cent., and 1 contained lead. Iron filings were present in several samples of tea. Many samples of "cream" confectionery were found not to contain genuine cream; 10 samples of mustard were adulterated with foreign starch; 60 samples of dried mint contained foreign leaves; facing was present in samples of barley, and 32 samples of rice contained talc and other mineral matter, dirt, acari or weevils. Adverse reports on 24 samples of fish were due to misrepresentation of names. A sample of cherry brandy was a cherry-flavoured beverage with no alcohol; dried peas contained arsenic and lead; aerated waters, cider, and canned peas and beans contained copper, and lead was found in curry powder, aerated waters and canned fish. Tin was present in canned fruit and vegetables and fish, and a sample of tinned sild contained both tin and zinc.

DRUGS.—Of 5886 samples, 286 were reported against. Thirty-two samples of sweet spirits of nitre were mostly deficient in ethyl nitrite; 16 samples of camphorated oil in camphor; iodine solution in alcohol, iodine or potassium iodide; boric ointment in boric acid; mercury ointment in mercury, and zinc ointment in zinc oxide. Calomel ointment was made with benzoated lard; a boric acid consisted of citric acid, and 2 samples of borax contained, respectively, 20 and 50 p.p.m. of arsenic. Nine samples of "lysol" were reported against, as they contained, instead of the 50 per cent. by volume of cresol of the B.P. standard, less than 3 per cent. The samples adversely reported on also included ammoniated tincture of quinine, ammoniated quinine tablets, Seidlitz, Gregory and grey powders, and bicarbonate of soda. D. G. H.

ALUMINIUM IN FOOD*

IN this Report information available upon the subject of aluminium in food has been collected and examined, with a view to reaching definite conclusions whether or not the metal is in any way injurious to health.

OCCURRENCE OF ALUMINIUM IN NATURE.—The proportion of aluminium in the earth's crust is estimated to be between 7 and 8 per cent. In agricultural soils it is usually less than this. Eight samples of soil from fields in various parts of England were found by the author to contain from 1·1 to 5·9 per cent., calculated on the dry soil. Aluminium is not a general constituent of plants, although in a

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* Reports on Public Health and Medical Subjects, No. 78. By G. W. Monier-Williams, O.B.E., Ph.D., F.I.C. Pp. 34. London: H.M. Stationery Office. 1935. Price 9d. net.

few plants (*e.g.* certain club mosses, *Lycopodium clavatum* and *L. complanatum*) it is present in considerable amount. The conclusion is drawn that much of the aluminium found in plants by different workers is the result of adventitious contamination with soil and dust. Much of the aluminium found in food is also probably due to contamination with soil and dust. Coffee beans were found, by the method described below, to contain 72 p.p.m. of aluminium, but none at all after prolonged shaking with soap and water. The amount of aluminium consumed daily with food which has been properly cleaned is very small (*e.g.* 5 to 10 p.p.m.). Human and animal tissues normally contain extremely small amounts of aluminium (1 to 2 p.p.m. in all organs).

ANALYTICAL METHODS.—The chief methods, other than spectroscopic, that have been used for determining aluminium in biological material are shown in outline in a diagram. In general, the problem is one of determining minute amounts of aluminium in a precipitate of mixed iron and aluminium phosphates. The modification of the colorimetric method used by Lampitt and Sylvester (ANALYST, 1932, **57**, 418) has given good results in the author's hands, although, in his opinion, colorimetric methods are less trustworthy than precipitation of the aluminium with 8-hydroxyquinoline.

The following method, depending on precipitation with 8-hydroxyquinoline, has been worked out:—A weighed quantity of the sample (25 to 100 g.) is dried and charred in a silica dish, and the char is treated with about 10 ml. of *N* sulphuric acid, dried and ashed at a low temperature in a muffle furnace. The sulphated ash is extracted on the water-bath with successive small quantities of dilute hydrochloric acid, any insoluble residue being filtered off and washed with hot water, the filter and its contents ignited in a platinum dish, the residue fused with 0·5 g. each of potassium and sodium carbonates, and the fused mass dissolved in hydrochloric acid and added to the main solution. This is evaporated in a silica dish, the residue is heated at 150° C. (to dehydrate any silica present), then cooled and extracted with moderately strong hydrochloric acid, and the liquid is filtered. The filtrate is boiled with a few drops of nitric acid (to oxidise iron) and evaporated to about 20 ml. If there is not sufficient iron present to impart a yellow tinge to the solution, 1 drop of 5 per cent. ferric chloride solution is added. If insufficient phosphoric acid is present to give an excess over that required to combine with the whole of the iron, ammonium phosphate (usually about 0·1 g. per 100 g. of sample) is added. The solution is transferred to a large boiling-tube, and dilute ammonia is run in from a burette until a slight permanent precipitate or turbidity is produced, leaving the liquid still acid (red or orange to thymol blue indicator). Three ml. of glacial acetic acid are added, the solution is heated just to boiling-point, and 5 ml. of 50 per cent. ammonium acetate solution are added gradually, with stirring, to complete the precipitation. The solution (which is now yellow) is transferred to a centrifuge tube, allowed to stand for 5 to 10 minutes, cooled and centrifuged. The supernatant liquid is decanted, the moist precipitate is shaken with hot water, cooled and again centrifuged, the mixed phosphates of iron and aluminium are dissolved in the minimum quantity of warm dilute hydrochloric acid, and the solution is diluted to about 15 ml. It is then treated with 1·25 ml. of glacial acetic acid and with 6·5 ml. of approximately 6 *N* sodium hydroxide solution (free from aluminium) to precipitate the iron as basic acetate, allowed to stand for 30 minutes, with occasional shaking, and centrifuged, the supernatant liquid being decanted. If the deposit of basic iron acetate exceeds 0·5 ml., it must be re-dissolved, the precipitation and centrifuging repeated, and the decanted supernatant liquids united.

The alkaline solution (containing the aluminium) is diluted to about 30 ml. and made just acid to bromthymol blue by adding dilute acetic acid. In the presence of 0·3 mg. of aluminium there will usually be a turbidity or precipitate of aluminium phosphate; this should be re-dissolved by adding powdered tartaric acid. Five ml. of 50 per cent. ammonium acetate solution are added, and the aluminium is precipitated by the gradual addition of a slight excess of 8-hydroxyquinoline acetate reagent [prepared by triturating 2·5 g. of the base with 5 ml. of glacial acetic acid, pouring the mixture into 100 ml. of water at 60° C., cooling and filtering (Lundell and Knowles, *Bur. Stand. J. Res., Wash.*, 1929, **3**, 91)]. Each ml. of the reagent precipitates about 1·4 mg. of aluminium. If more than 2 ml. are required, it is advisable to dilute the liquid to 50–60 ml. The solution is neutralised with diluted ammonia, and then made just acid with dilute acetic acid, after which the beaker is covered with a watch glass, heated to about 70° C. for 15 minutes, and allowed to stand at room temperature overnight. The precipitate is filtered off with the aid of suction, washed with small quantities of warm water, and dissolved in about 10 ml. of hot dilute (4 : 1) hydrochloric acid, and the solution is cooled and slowly titrated with 0·1 *N* bromine (bromide-bromate) solution, indigo carmine being used as indicator, and an excess of 0·5 to 1 ml. of bromine solution added. The exact excess is determined by adding potassium iodide and titrating with thiosulphate (starch as indicator): 1 ml. of 0·1 *N* bromine ≡ 0·000255 g. of aluminium. Sodium hydroxide solution should be kept in a bottle, the inner surface of which has been waxed.

The results of test analyses of various materials to which known amounts of aluminium had been added, gave results agreeing closely with the amounts taken. Under the conditions described, titanium, bismuth, tin and lead are the only common metals likely to be precipitated simultaneously with aluminium and iron phosphates. Titanium and bismuth are completely removed with the iron when this is separated as basic acetate. Tin and lead may be dissolved with the aluminium in dilute sodium hydroxide solution. Tin is not precipitated with 8-hydroxyquinoline in weakly acid solution. Lead gives a purple-brown precipitate which is much less insoluble than the greenish-yellow aluminium compound, but if the lead is present in much larger amount than aluminium, it must be removed by means of hydrogen sulphide before precipitating the mixed phosphates.

ACTION OF FOOD ON ALUMINIUM VESSELS.—The figures given by various workers for the amount of metal taken up by food from aluminium vessels vary considerably under different conditions. Thus the action of acids, when present in foods, appears to be much less than that of the pure acids alone.

In some experiments made for this Report, mutton broth containing mixed vegetables was cooked in an aluminium pan, and, after being sampled, was allowed to remain in the pan and re-heated on successive days. A similar mixture was cooked in an enamelled pan as a control. The results were as follows:

	Aluminium in broth p.p.m.
Cooked in enamelled pan ..	1·13
Cooked in aluminium pan—	
(i) Immediately after cooking	7·0
(ii) After 24 hours	10·6
(iii) After 48 hours	11·5

Several authors have drawn attention to the fact that corrosion of aluminium vessels becomes less during prolonged use and tends to reach a minimum, owing apparently to the formation of a resistant oxide coating. A process is, in fact, in operation for increasing this oxide coating to a thickness of 0·01 to 0·04 mm. by anodic oxidation (Elssner, *Chem.-Ztg.*, 1935, **59**, 213, 215).

The purity of the metal has some influence on its liability to corrosion. Commercial aluminium of 99·5 per cent. purity is more resistant than the aluminium formerly produced, which contained considerable amounts of iron and silicon.

BEHAVIOUR OF ALUMINIUM IN THE BODY.—The state in which aluminium may exist in the stomach contents probably varies with different conditions. It may be concluded that a considerable proportion of the aluminium taken into the stomach is soluble. The diffusibility of aluminium salts into the blood through the wall of the digestive tract appears to vary considerably with the circumstances. With regard to the effect on the digestive tract, a consideration of the recorded results indicates that, in reasonable doses, aluminium compounds do not make the normal person obviously ill within a period of weeks or months. The results of injection experiments cannot be deduced as evidence of toxicity when the substances in question are taken by the mouth. The general conclusion reached in the Report is that there is no convincing evidence that aluminium, in the amounts in which it is likely to be consumed as a result of using aluminium utensils, has a harmful effect upon the ordinary consumer. It is possible that there may be individuals who are susceptible to even such small doses of aluminium as may be derived from aluminium utensils, but evidence of this is inconclusive.

The Report concludes with an alphabetical list of 292 references.

Trinidad and Tobago

ADMINISTRATION REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1934

IN his Annual Report the Government Analyst (Mr. H. S. Shrewsbury) states that the work undertaken for the various departments of Government involved the examination of 4074 samples, 1497 of which consisted of foods.

"PHALKA GHEE."—A sample sold as "ghee," required by the Food and Drugs Ordinance to consist of pure butter-fat, was found to consist of an inferior vegetable fat known as "Phalka ghee" (meaning vegetable butter, and an obvious misnomer). So-called "Phalka ghee" is obtained from the seeds of various *Bassia* species, and is itself frequently adulterated with fats other than *Bassia*, such as coconut, arachis, cottonseed, safflower, sesame and niger seed oils; mahua, salvadora and castor oil are also sometimes used as adulterants, the last three being considered injurious.

ADULTERANTS OF COFFEE.—Of 157 samples of coffee, 24 were adulterated, the adulterants being burnt sugar, roasted pigeon peas and split pigeon peas (stated to be derived from varieties of the same plant); sometimes all three adulterants were present.

CAMPAIGN AGAINST VAMPIRE BATS.—The Department was able to assist the Medical Department in their campaign against vampire bats, considered to be the carriers of paralytic rabies in man and beast. The haunts of these bats are partly discovered by means of the excrement left therein; the excrement of vampire bats contains blood, very largely digested. The detection of blood therein serves to distinguish the excrement of vampire bats from that of all other species. It was for this purpose that 16 specimens of bat excrement were submitted by the Acting Medical Inspector of Health. Some of these were found to contain blood, proving the presence of vampire bats in the particular haunts from which the specimens were taken. It is useful to be able to detect the presence of vampire bats as distinguished from that of other species of bats, because whilst there is some hope of exterminating such a peculiar species as the vampire, and thus terminating the disease of paralytic rabies, it is impossible to exterminate all species of bats, and efforts made in this direction, instead of concentrating on the vampire, simply delay the time when the Island may possibly be completely rid of paralytic rabies. It has always been a very difficult matter to exterminate even a single species of animal.

Georgia Experiment Station

FORTY-SEVENTH ANNUAL REPORT, 1934–1935

THE Report of the Director of the Station for the year 1934–1935 gives a survey of all the agricultural research work carried out in the State of Georgia, including the co-operative research with State and Federal agencies. Subjects investigated by the Chemistry Department include the following:

BORON AND COTTON NUTRITION.—Cotton nutrition study, carried out in water culture, was designed to determine the influence of the source of nitrogen upon the boron requirements of the cotton plant. Although the results obtained were not conclusive, they did indicate that there is little difference in the boron requirements of this plant regardless of whether ammonium- or nitrate-nitrogen is used. The results indicate that cotton has a high requirement and a high tolerance for boron, but that growing conditions have considerable influence on its effects on the plant. The results of this experiment also emphasise the need for more exact control of conditions in studies of this type. Contrary to results reported by other investigators, the presence of boron in the culture medium, and its consequent absorption, did not reduce the absorption of either calcium or magnesium. Evidence obtained indicates that there is but little relation between the concentration of boron in the culture solution and the amount of boron absorbed by the plant.

FREEZING PRESERVATION OF FRUITS AND VEGETABLES.—A study of the reaction of different types of plant tissue to freezing was made. Evidence was obtained which indicates that the age and structural form of tissue have great influence on the reaction to freezing. The indications are that the variations in the reaction of different tissues to the freezing process are largely physical. In addition to its connection with freezing-preservation of fruits and vegetables, this study has a direct bearing on the use of expressed saps in the metabolism studies of plants.

UTILISATION OF PIMIENTO* WASTE.—The principal red pigment of the Perfection pimiento has been isolated and identified as capsanthin. Previous studies have shown that colour development in egg-yolks follows within a very few days after the introduction of pimientos into the feed of the hen. Later studies have shown that the colour-effect of the pimiento on the egg-yolk disappears very slowly after the removal of pimiento from the feed. The pigment also seems to disappear from the body tissues much more slowly than it is deposited. In feeding experiments in which quantities of 0·4 g. and 3·0 g. of Perfection pimiento per 90 g. of basal diet were given to hens, the vitamin *A* content ranged from 20 to 40 units per g. of yolk.

Pimientos and Milk.—Two Holstein cows were fed on a low vitamin *A* ration for three months and until symptoms of vitamin *A* deficiency were apparent. The ration was then supplemented with dried pimientos for three weeks, and the increase in the vitamin *A* content of the milk was determined. All samples were kept frozen for several months before the biological tests were made. The amount of vitamin *A* in the milk after the pimiento feeding was three-fold that of the pre-feeding period.

VITAMIN *G* [B_2] IN PIMIENTOS.—The vitamin *G* content of pimientos is evidently low. Upon the highest level fed, namely, 1 g. of canned product per day, the rats failed to gain weight during an experimental period of five weeks.

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* In this country pimiento is understood to refer to allspice, and pimento to capsicum varieties.—EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Composition of Commercial Dried Whey. W. L. Davies. (*J. Soc. Chem. Ind.*, 1935, **54**, 338–341T.)—Nineteen samples of dried wheys of good quality, ranging in colour from rich cream to dark brown, which had been stored for a number of years, were analysed in detail, with the following results:—Moisture varied from 3·1 to 11·7 per cent., including at least 0·3 to 8·2 per cent. of "free" or hygroscopic moisture; ethereal extract was nil to 2·01 per cent.; ash was 7·03 to 8·37 per cent. on the dried whey, the chloride-content averaging for 15 samples 2·28 per cent., giving a saline taste to the whey, and in most cases affording means of identifying dried whey from dried skim or whole milk. The amounts of calcium and phosphorus were found to vary, and increased amounts appear in whey as the colour darkens. The average crude protein-content (N × 6·38) of 18 samples was 12·5 per cent., so that there does not appear to be any appreciable loss of nitrogen during drying. The true protein varied from 53·8 to 71·6 per cent. of the crude protein, which corresponds with a higher amount of non-protein nitrogen than is to be expected from the normal nitrogen distribution in milk, perhaps owing to partial hydrolysis of the soluble protein in acid whey during heating and drying. Usually the amount of protein rendered insoluble during drying was, roughly, half the true protein. Titratable acidity varied, as a rule, between 1·7 and 3·3 per cent. (as lactic acid), averaging 2·38 per cent.

D. G. H.

Nitrogen Distribution and Carbohydrate Partition in Philippine Rice Bran. J. Marañon and L. Cosme. (*Philippine J. Sci.*, 1935, **57**, 289–294.)—A high-grade rice bran known locally as "tikitiki" or "darak," obtained immediately after milling from a Manila mill, was found to have the following percentage composition:—Moisture, 11·65; fat (ethereal extract), 19·81; protein (nitrogen, 2·26 per cent.), 12·50; ash, 10·41; crude fibre, 6·32; and carbohydrates (by difference), 39·31. Nitrogen distribution was then determined; non-protein nitrogen by the method of Puchner, Leavenworth and Vickery (ANALYST, 1930, **55**, 406); protein nitrogen according to Stutzer's method (Leach and Winter, *Food Inspection and Analysis*, 4th Ed.); water-soluble nitrogen and free amino acid nitrogen by Van Slyke's method (*J. Biol. Chem.*, 1912, **12**, 275). The nitrogen partition after acid hydrolysis was carried out according to Jodidi and Moulton's procedure (*J. Amer. Chem. Soc.*, 1919, **41**, 1526). Calculated on the basis of total nitrogen on the moisture-free sample containing 2·264 per cent. nitrogen, the percentage proportions of nitrogen found were:—Non-protein, 11·44; protein, 88·56 per cent. The percentage distribution of the non-protein nitrogen was: acid amide, 1·68; humin, 0·93; basic, 1·37; and non-basic, 7·46; and that of the protein nitrogen, acid amide, 7·68; humin, 2·43; basic, 15·02; and non-basic, 63·43. The water-soluble nitrogen was 19·52 per cent. After acid hydrolysis the nitrogen distribution, calculated as before, was found to be: acid amide, 9·36; humin, 3·36; basic, 16·39; and non-basic, 70·89 per cent. The nitrogenous substances in rice bran thus consist mostly of protein, which is composed largely of non-basic nitrogen. Carbohydrate distribution (calculated on a basis of total carbohydrate on the moisture-free sample containing 51·65 per cent. total carbohydrates, including fibre) was as follows:—Reducing sugars, 0·87; non-reducing sugars, 11·66; starch, 46·76; dextrin, 1·01; hemicellulose, 1·61; pentosans, 17·58; crude fibre, 13·85; gums, 5·64; and undetermined, 1·02 per cent.

D. G. H.

Rate of Formation of Fully-saturated Glycerides during Hydrogenation of Different Natural Fats. T. P. Hilditch and H. Paul. (*J. Soc. Chem. Ind.*, 1935, **54**, 336–338T.)—Of the 6 fats studied, rape seed, olive and cottonseed oils conform closely, on the whole, to the "even-distribution" type of mixed glyceride, and this group would also include the Cape Palmas palm oil, whereas the Belgian Congo palm oil is less homogeneously built with a probably more complex configuration of the mixed glycerides, and the pig-back fat represents a somewhat different type. The proportions of (*a*) total saturated acids (per cent. mol.), and (*b*) palmitic acid (per cent. mol.) in the fats were as follows:—Rape seed oil (*a*) 3, (*b*) 2; olive, (*a*) 14, (*b*) 12; cottonseed (*a*) 27, (*b*) 25; pig-back fat, (*a*) 44, (*b*) 30; Cape Palmas palm oil, (*a*) 41, (*b*) 36; and Belgian palm oil, (*a*) 50, (*b*) 45. The hydrogenation data, reproduced on a curve, show that for a given total content of saturated acids, hydrogenated rape oil has the highest proportion of completely saturated triglycerides, followed in descending order by hydrogenated olive, cottonseed, pig-back fat and the two palm oils. On comparing the proportion of fully-saturated acids which have actually been produced from unsaturated acids present in the original fat, using as abscissae the molar amounts of saturated acids calculated as a percentage of the total unsaturated acids in the original fat, it will be found that the order of the curves is the exact opposite of the first picture, the Belgian Congo palm oil yielding the highest proportion of fully-saturated glycerides for a given degree of partial hydrogenation. The pig-back fat, with a content of palmitic acid somewhat less than that in the Cape Palmas palm oil, is quite out of line with the vegetable fat series. If, however, the data for this fat are plotted as fully-saturated glycerides in the hydrogenated fats against the total C_{18} acids present in the original fats, a curve results which falls exactly into position with that of the vegetable series, confirming the view in favour of the hypothesis that the palmito-stearo-glycerides of animal depôt fats have been produced as the result of partial reduction *in situ* of pre-formed palmito-oleo-glycerides.

D. G. H.

Oil of *Cassia absus*. Z. Ahmad. (*Z. Unters. Lebensm.*, 1935, **70**, 166–169.)—The seed-kernels of *C. absus* (Linn.) are largely applied in India as a household remedy in cases of eye trouble. The whole seeds yield 4 per cent. of dark green oil, and the kernels 6 per cent. of golden-yellow oil. The constants for the whole seed (kernel) oil are: sp.gr. at 26° C., 0·9276 (0·9284); n^{20}, 1·4840 (1·4735); saponification value, 190·4 (185·6); iodine value (Wijs), 130·5 (125·7); acetyl value, 12·0 (10·8); acid value, 2·5 (1·4); unsaponifiable matter, 8·4 (4·8) per cent. The fatty acids of the whole seed oil have: mean molecular equivalent, 282·4;

iodine value, 129·2; saturated acids 19·0, and unsaturated acids 81·0 per cent. The probable percentage composition of this oil is: oleic acid, 16·32; linolic, 47·32; linolenic, 0·41; hydroxy-acids, 0·75; palmitic, 6·28; stearic, 8·10; lignoceric acid, 0·82; unsaponifiable matter, 8·40; glycerol, 10·40; undetermined, 1·20. The oil contains a saturated hydrocarbon in small amount, and 0·11 per cent. of phytosterol. T. H. P.

Composition of Szegeder Edelsüss Paprika Meal Products. I. Horváth. (*Z. Unters. Lebensm.*, 1935, **70**, 195–201.)—This material, which is the most important Hungarian spice, consists of a ground mixture of the ripe, red fruits of paprika with a proportion (varying) of the fruit husks and seeds which have been purified by washing and mechanical treatment. The colour varies from dark red for products containing much seed to pale red for those with relatively little seed. The mean percentage compositions of a number of deep red, bright red, and pale red samples were found to be:—Loss at 100° C., 8·2, 7·8, 10·7; ash, 5·32, 5·74, 6·06; sand, 0·27, 0·24, 0·17; ether extract, 15·77, 13·34, 12·25; petroleum spirit extract, 14·37, 12·45, 11·28; nitrogen, 2·45, 2·39, 2·37; crude protein, 15·29, 14·97, 14·81; sugar as invert sugar, before inversion, 12·51, 13·71, 14·84; ditto, after inversion, 13·48, 14·53, 15·57; crude fibre, 23·16, 23·86, 23·16; essential oil, 0·085, 0·135, 0·113. The methods of analysis are briefly outlined. T. H. P.

Nicotine-content of Tobacco Smoke. C. O. Jensen and D. E. Haley. (*J. Agric. Res.*, 1935, **51**, 267–276.)—Methods of determination of nicotine are reviewed, and a modification of Chapin's procedure (*U.S. Dept. Agr., Bur. Animal Indus. Bull.*, 1911, 133) is recommended. Preliminary experiments showed that with solutions containing less than 0·02 per cent. of pyridine there is little interference with the method as normally applied to cigarette smoke, and that ammonia also is without influence on the results. An apparatus is described for "smoking" the cigarettes, in which the sample is held in one end of a calcium chloride tube, the other being connected through 4 absorption vessels in series with a vacuum pump with a slowly-rotating valve. The cigarettes were stored for 2 weeks under conditions of standard humidity, and 5 were then weighed and smoked with puffs lasting 1·6 seconds, with intervals of 6·1 seconds between puffs; 20 ml. of air passed through the cigarette at each puff into the absorbing vessels, each of which contained 12·5 ml. of chloroform and 12·5 ml. of 0·1 *N* sulphuric acid. The cigarette-holder and the vessels were washed with chloroform and water, and the aqueous layer from the bulked washings and absorption solutions (containing nicotine sulphate) was steam-distilled in the presence of 35 ml. of sodium hydroxide solution, the distillate, which amounted eventually to 500 ml., being collected in water and acidified with 15 ml. of 25 per cent. hydrochloric acid. The nicotine was then precipitated with 5 ml. of 12 per cent. silicotungstic acid, and on the next day it was filtered through a weighed Gooch crucible which was subsequently heated at 125° C. for 3 hours and re-weighed. Experiments with tobaccos containing 0 to 24·44 per cent. of moisture showed that the percentage of nicotine in the smoke, compared with that present in the tobacco (respective values, 42·4 and 21·2 per cent.), varies inversely as the moisture-content. A decrease in the strength of the puff (corresponding with the passage of 16 ml. of air through the cigarette) decreased the percentage of nicotine in the smoke. Studies of the amount of nicotine in the unsmoked butt were made by coating this portion with paraffin wax and inserting it in the warm glass holder, so that, on cooling, the wax made an air-tight joint. Cigarettes 7 cm. long (moisture, 11·1, and nicotine, 2·17 per cent.) were smoked until butts 1 and 3 cm. long remained, and the nicotine in the butt was calculated from the formula $100\ (5{\cdot}7\ F-A)/5{\cdot}7\ F$, where A is the amount of nicotine in the smoke per cigarette whose dry weight equals 1 g., and F is the fraction of the cigarette smoked; values found were 22 and 60 per cent., respectively. Investigations on the "side-stream" smoke were made by placing the cigarette loosely in an opening (slightly larger in diameter than the cigarette) in a bulb, the smoke being drawn out continuously through an opening in the opposite side of the bulb into the absorbing vessels. The percentages of nicotine in the main and side streams (compared with the total nicotine in the tobacco) were, respectively, 26·3 and 31·8 for a moisture-content of 11·13 per cent., and 42·4 and 28·6 for bone-dry tobacco. This apparent contradiction of some of the results given above may be explained partly by the fact that dry cigarettes burn more rapidly than moist tobacco, so that in the former case there is more distillation and less destruction of the nicotine. J. G.

Occurrence of Hydrogen Sulphide in Tobacco Smoke. A. Wenusch. (*Z. Unters. Lebensm.*, 1935, **70**, 201–204.)—The proportion of hydrogen sulphide in tobacco smoke depends not only on the nature of the tobacco, but also on its method of preparation and on the way it is smoked. Cigarettes of oriental tobacco usually yield less hydrogen sulphide than cigars, and the sulphide increases in quantity with the rate of smoking. With intermittent smoking, a sample of cigars gave 0·019 per cent., and Memphis cigarettes 0·007 per cent. of hydrogen sulphide. Evidence is cited in disagreement with Vogel's view that the sulphide is derived from sulphuric acid pre-existing in the tobacco (*Dingler's Polytechn. J.*, 1858, **148**, 231). A more probable source is the protein of the tobacco. The hydrogen sulphide contributes to the aroma of the smoke, but is insufficient in amount to have toxicological importance. T. H. P.

Biochemical

Carcinogenic Hydrocarbons and their Relationship to the Sterols. J. W. Cook. (*Chem. Weekblad*, 1935, **32**, 563–566.)—Earlier work on the carcinogenic effects of coal tar and similar products is reviewed; the results indicate that the active substance is a hydrocarbon, and is responsible for the bands 400·0, 418·0 and 440·0$m\mu$, which are common to the fluorescence spectra of many carcinogenic mixtures. The strong fluorescence of anthracene suggested the synthesis of homologues and benzologues of 1·2-benzanthracene, in the hope of finding a compound which would reproduce these spectral characteristics, and the results obtained are summarised in the present paper. *Tetracylic and Pentacylic Aromatic Hydrocarbons.*—Of the 15 hydrocarbons with 5 condensed benzene rings which are theoretically possible, 12 have been examined, but only 1.2.5.6-dibenzanthracene and 1.2-benzopyrene were found to have any pronounced activity. Of the

6 possible hydrocarbons with 4 condensed benzene rings, chrysene and 3.4-benzophenanthrene were slightly active, the latter being the simplest carcinogenic chemical compound known, and the only one not related to 1.2-benzanthracene. *Derivatives and Homologues of 1.2-Benzanthracene.*—Activity is usually evident when there are substituents at positions 5 or 6, or both, but rarely in other cases; substitution at position 5 is the more effective in inducing carcinogenic activity. Data given in support of these generalisations show the numbers of epitheliomas and papillomas produced in a given time in mice for the various derivatives. With the exception of 5.6-*cyclo*penteno-1.2-benzanthracene, none of the numerous simple derivatives and homologues of 1.2.5.6-dibenzanthracene examined had a greater activity than the parent substance, substitution in the *meso*-position or reduction of the ring-system being particularly effective in reducing the carcinogenic power. *Coal-tar Carcinogens.*—The fluorescence spectrum was used as a method of control in the fractional distillation of 2 tons of coal-tar pitch, and in this way it was possible to select fractions which, after extraction with solvents and crystallisation of the picrates, yielded a few g. of a substance which was identified by synthesis as 1.2-benzopyrene. Since both the synthetic and isolated products had the characteristic fluorescence spectra associated with carcinogenic materials (cf. *supra*), and produced tumours in about half the time required by 1.2.5.6-dibenzanthracene, it is assumed that 1.2-benzopyrene is the principal, but not necessarily the only carcinogenic substance in coal tar. *Carcinogens derived from the Bile Acids.*—The introduction of the Rosenheim-King formulation for the bile acids (1932) suggested a structural relationship with the carcinogenic hydrocarbons, because the side-chain of the sterol-bile acid molecule is in such a position that cyclisation leads to a hydrogenated 1.2-benzanthracene ring-system. Thus, oxidation and then reduction of de-oxycholic acid yields 12-ketocholanic acid, which is converted into dehydro-norcholene by thermal dehydration and decarboxylation. This, in turn, may be dehydrogenated, in the presence of selenium, to form the aromatic hydrocarbon methylcholanthrene, a 5.6-substituted derivative of 1.2-benzanthracene and the most active carcinogen yet encountered; thus, a 0·3 per cent. solution in benzene produced tumours in the skin of mice after 75 days. Recent work on the structure of the hormones has shown them to be biological degradation products of cholesterol differing in the degree of hydrogenation of the ring-system, and it is therefore inferred that some enzymic factor in the body may be capable of effecting dehydrogenation of the sterol ring-system. Excessive activity of this factor may possibly contribute to the production of carcinogens *in vivo*. J. G.

Titration of Fluorine in Biological Materials. E. W. Scott and A. L. Henne. (*Ind. Eng. Chem.*, *Anal. Ed.*, 1935, 7, 299–300.)—*Ashing.*—To samples of tissues (*e.g.* heart, lungs, spleen, etc.), solid lime or lime water, as appropriate, is added, and the whole is well dried in a silica basin for several days at a "medium temperature." No lime addition is made with teeth or bones. The bulk of fat-containing samples is burned by inserting a wick and igniting while hot. The dried sample is ashed for 12 to 24 hours at 600° C. Teeth or bones require about 48 hours at 650–700° C. Fusion of sample (*e.g.* of liver) indicates insufficient lime addition. The residue is finely ground in a mortar. *Separation of Fluorine.*—The ash (1 g.) is decomposed with perchloric acid and the fluorine is distilled off as hydrofluosilicic acid by the method of Willard and Winter (*Ind. Eng. Chem., Anal. Ed.*, **1933**, **5**, 7, Abst., ANALYST, **1933**, **58**, 242). *Titration of Fluorine.*—The volumetric method proposed by Willard and Winter was not found satisfactory, and the following method was adopted: To the distillate, a few drops of 0·04 per cent. phenol red solution are added; the solution is neutralised with sodium hydroxide and evaporated to a volume of 2 to 3 ml., additions of 0·01 *N* perchloric acid being made meanwhile from time to time to maintain neutrality. Two drops of a saturated alcoholic solution of methyl red and 10 drops of 0·04 per cent. aqueous bromocresol green solution (exactly neutralised with sodium hydroxide) are added. The liquid is titrated at 80° C. to the "maximum red colour" with cerous nitrate solution (1 ml. ≡ 0·5 mg. of fluorine; method of standardisation not specified). When the amount of fluorine is less than 0·2 mg., thorium nitrate solution (1 ml. ≡ 0·1 mg. of fluorine) may be substituted for the cerous nitrate, the same mixed indicator being used; it was found necessary to make a deduction of 0·02 mg. of fluorine in the determination of these small amounts. In test experiments the ash was divided into two parts, to one of which was added a known amount of calcium fluoride. Determination of fluorine in the two portions gave differences corresponding closely with the added calcium fluoride. S. G. C.

Metabolism of the Phospholipids. The Passage of Elaidic Acid into Tissue Phospholipids. R. G. Sinclair. (*J. Biol. Chem.*, 1935, **111**, 515–526.)—Elaidic acid may comprise one-third of the total fatty acids in the phospholipids of the liver and skeletal muscles of rats which have been raised on a diet rich in elaidin. When adult rats which have been raised on ordinary diets are fed with elaidin, elaidic acid may replace 25 to 30 per cent. of the natural fatty acids, chiefly the fully-saturated acids. The rate of appearance of elaidic acid in, and disappearance from, the phospholipids is rapid in the liver and slow in muscle. This process is practically complete in the liver in one day, but many days are necessary for the muscle. From the factors governing both the degree of unsaturation of the phospholipids and the rate of turnover of elaidic acid it is suggested that at least two classes of phospholipids exist. One class consists of the more highly unsaturated phospholipids, and is concerned in the essential make-up of the cell; the other class consists of the less unsaturated compounds, and is an intermediate product in fat metabolism. Both classes are present in the liver, but the non-metabolic type is the important one in skeletal muscle. S. G. S.

Use of a Closed Titration Flask in the Bromometric Determination of Magnesium with 8-Hydroxyquinoline in Tissues and Urine. D. M. Greenberg, C. Anderson and E. V. Tufts. (*J. Biol. Chem.*, 1935, **111**, 561–565.)—The magnesium precipitate is dissolved in strong hydrochloric acid and washed into a suction flask whose side tube is plugged with cotton wool. The mouth of the flask is then closed with a paraffined cork stopper which carries a funnel having a stem long enough to reach below the level of the liquid in the flask. Bromination is carried out in this flask, then potassium iodide is added, and the liberated iodine titrated in the same vessel. In the determination of magnesium in urine, 10 ml.

are adjusted to *p*H 5·0–5·5, heated with 5 ml. of 4·5 per cent. potassium oxalate and diluted to 50 ml. After filtration an aliquot portion is used for the determination. If the urine contains protein, this must be removed by treatment with trichloroacetic acid and the filtrate used for the oxalate precipitation. Tissues should be dried and ignited, and the ash dissolved in *N* hydrochloric acid and treated in a similar manner. Iron may be removed by precipitation with hydroxyquinoline at *p*H 5·0 (Alten, Wieland and Kurmies, *Z. angew. Chem.*, 1933, **46**, 697), after which the magnesium is precipitated by the method previously described. (Greenberg and Mackey, *J. Biol. Chem.*, 1932, **96**, 419; ANALYST, 1932, **57**, 730.) S. G. S.

New Method for the Determination of Minute Amounts of Lead in Urine. J. R. Ross and C. C. Lucas. (*J. Biol. Chem.*, 1935, **111**, 285–297.)—The urine (100 ml. or more) is adjusted to *p*H 4·5 in a suitable glass-stoppered tube by the addition, in drops, of glacial acetic acid. Approximately 0·5 g. of powdered ammonium oxalate is then added and mixed with the solution. This is followed by 2 ml. of 10 per cent. calcium chloride solution, again with thorough mixing. The lead is, in this way, completely precipitated by entrainment with the calcium oxalate precipitate. After the mixture has stood for at least 20 minutes with occasional shaking, the open end of the tube is covered with a cigarette paper held in place by a rubber band and the tube is centrifuged. The supernatant liquid is discarded, and the precipitate is washed with about 20 ml. of double-distilled water containing a few drops of saturated ammonium oxalate solution. The precipitate of calcium oxalate and uric acid is broken up with a glass rod, and the whole is again centrifuged. After the wash-water has been decanted, the tube is inverted and allowed to drain on filter-paper. This removes most of the phosphates, which otherwise would interfere later in the procedure. The precipitate is next treated with 2 ml. of perchloric acid and 2 drops of 30 per cent. hydrogen peroxide, and the mixture is heated for at least 20 minutes. To the hot mixture 3 drops of strong hydrogen peroxide are added cautiously, and the heating is continued for 3 minutes. After cooling, 5 ml. or more of double-distilled water are added, followed by 3 ml. of 10 per cent. citric acid solution, to prevent the precipitation of traces of phosphates which may be present. The solution is then made just alkaline by the careful addition of concentrated ammonium hydroxide solution, bromothymol blue being used as the indicator. If it is made too alkaline a precipitate will form, and this must be dissolved in citric acid. The whole, or an aliquot part, of the solution is transferred to a 50-ml. separating funnel, and 4 drops of 20 per cent. sodium cyanide solution are added. The volume at this point should be about 20 ml. The mixture is then shaken vigorously with about 1 ml. of purified dithizone solution. The cherry-red solution of lead dithizone in carbon tetrachloride is drawn off, and the extraction is repeated with 1-ml. or diminishing portions of the dithizone solution until no further red colour appears. The mixed red dithizone solutions are washed with 10 ml. of 0·5 per cent. ammonium hydroxide solution containing 2 or 3 drops of sodium cyanide solution, made up to a definite volume with carbon tetrachloride, and compared with a standard lead solution in a colorimeter. It is sometimes preferable to shake the red solution with dilute (1 : 3) hydrochloric acid and compare the green colour so formed. The purified dithizone solution is prepared by dissolving about 4 mg. of commercial dithizone in 25 ml. of carbon tetrachloride. This is extracted three times with 25 ml. of 0·5 per cent. ammonium hydroxide. The carbon tetrachloride layer is rejected and the aqueous layer is neutralised to litmus with $N/1$ hydrochloric acid solution. This is then extracted with 15-ml. portions of carbon tetrachloride, which are united, diluted to 100 ml. and kept in a refrigerator. This solution will last for 3 days. The recovery of lead added to urine was such that the accuracy appears to be ± 0·004 mg. of lead for amounts up to 0·10 mg. Normal urine was found to contain 0·05 mg. per l. for adults and 0·06 mg. per l. for children. Urine from lead workers contained up to 0·64 mg. per l. S. G. S.

Determination of the Pectolytic Power of Filtration Enzymes. A. Mehlitz and H. Maass. (*Z. Unters. Lebensm.*, 1935, **70**, 180–186.)—The clearing of fruit juices and sweet musts depends fundamentally on the removal of the pectin. This may be effected spontaneously by means of pectase present in the juice, or, very incompletely, by treatment with tannin and gelatin, the precipitate formed then adsorbing the pectin. Both of these methods are surpassed by Mehlitz's process, which makes use of so-called filtration enzyme preparations, these hydrolysing the pectin to a finely dispersed form and converting this into monogalacturonic acid in a state of true solution. The method previously given for determining the pectolytic power of these enzyme preparations (*ibid.*, 1934 **68**, 96) has certain disadvantages, and is now replaced by the following procedure: 200 ml. of a pectin solution yielding about 2 (1·7 to 2·3) g. of calcium pectate, and having *p*H 3·6, are mixed for 5 minutes with 1 g. of the enzyme preparation in a 250-ml. flask with a ground stopper. The flask is kept for 15 hours in a thermostat at 37° to 38° C., after which 10 ml. of 40 per cent. (vol.) formaldehyde solution are added, and the stopper is at once replaced. The liquid is cooled and filtered through a pleated paper, 25 ml. of the filtrate being transferred to a 250-ml. measuring flask and made up, with frequent swirling, to the neck of the flask, with water at 80° C. After being cooled, the solution is made up to 250 ml. and mixed. Ten ml. of the liquid are mixed with 80 ml. of water and 10 ml. of N sodium hydroxide in a 400-ml. wide-form Jena beaker, which is covered, and left at least 7 hours, 50 ml. of N acetic acid and 50 ml. of $2\ N$ calcium chloride solution being then added. The whole is boiled for about 3 minutes, and the calcium pectate precipitate is collected on a weighed filter (Schleicher and Schüll, No. 589, 11 cm. diameter), and washed with hot water until it gives no reaction with silver nitrate. The paper and precipitate are dried at 105° C. until constant in weight (at least 6 hours). The weight of the precipitate is multiplied by 1·05 to correct for dilution of the solution with the formaldehyde, and the weight thus obtained is subtracted from that of the calcium pectate given by 10 ml. of the original, unfermented solution. Multiplication of this remainder by 5 gives the pectolytic activity in Mehlitz units. T. H. P.

Method for the Direct and Quantitative Study of Amyloclastic Activity of Amylases. M. L. Caldwell and F. C. Hildebrand. (*J. Biol. Chem.*, 1935, **111**, 411–420.)—The method is based upon the direct determination of residual starch or amylose at any stage in its hydrolysis, and depends upon quantitative precipitation, free from dextrins and maltose, by ethyl alcohol. To the solution of starch or amylose dispersion, sufficient alcohol is added to give a final concentration of 55 per cent. by volume. The mixture is stirred vigorously by hand, and a flocculent white precipitate is formed fairly quickly. This is allowed to settle, and the supernatant liquid is decanted through a Gooch crucible containing a thin mat of asbestos and half filled with fluffy asbestos, which (with the crucible) has previously been heated to constant weight in a muffle-furnace. The precipitate is washed by decantation, twice with 55 per cent. and twice with 70 per cent. alcohol. The washed precipitate is finally transferred to the crucible with a jet of 96 per cent. alcohol and washed with a mixture of equal volumes of 96 per cent. alcohol and ether. The crucible is then dried to constant weight at 105° C., cooled and weighed. The crucible may be used again, if, after each determination, it is heated at a low red heat for 3 hours. S. G. S.

Remarks concerning the New Colour Reaction of Vitamin *A*. E. Rosenthal and J. Erdélyi. (*Biochem. J.*, 1935, **29**, 2112–2113.)—In the colour test for vitamin *A*, which was first described by these authors in 1934 (*Biochem. J.*, 1934, **28**, 41; ANALYST, 1934, **59**, 562), the use of alcohol-free chloroform is recommended. With the use of guaiacol, as suggested, it is unnecessary to warm the reaction mixture, as the colour produced in the cold is quite stable and can be compared with that of a freshly-prepared dilute solution of potassium permanganate. Warming the reaction mixture is necessary only if it is desired to demonstrate vitamin *A* in the presence of carotene. S. G. S.

Observations on the Estimation of Ascorbic Acid by Titration. E. W. McHenry and M. Graham. (*Biochem. J.*, 1935, **29**, 2013–2019.)—The following modifications in the titration of ascorbic acid by 2 : 6-dichlorophenolindophenol were used. The indicator was prepared in a phosphate buffer solution at *p*H 7·2. A secondary standard, consisting of a slightly acid solution of ferrous ammonium sulphate, was used, which was kept for 6 months without loss in an atmosphere of nitrogen in an automatic burette. This was standardised against ascorbic acid through the medium of the indicator solution. In order to avoid the error caused by the reduction of the indicator by acid, the indicator solution was diluted with 15 to 20 volumes of water just prior to the titration. It was found that, with solid foods, at least three extractions with trichloroacetic acid were necessary, but that a 3 per cent. acid solution gave less destruction than the usual 5 per cent. The addition of a few drops of potassium cyanide solution during extraction also stabilised the ascorbic acid present. An increase in the volume of the extraction solution was found to give increased accuracy. Where the plant pigment was insoluble in chloroform it was found that interference from this source was avoided if this solvent was added to the titration flask. The tip of the burette was lowered into the chloroform, and the aqueous layer was stirred by bubbling carbon dioxide through it without disturbing the chloroform layer. Where the plant pigment was soluble in chloroform it was found possible to extract it with butyl or amyl alcohol. This was then washed with water, and the aqueous solution was added to the acid extract. The loss by this method was insignificant.

Vegetable tissues generally contain appreciable amounts of reversibly oxidised ascorbic acid, for they do not appear to possess a mechanism which prevents the aerobic oxidation of ascorbic acid. Some of the vegetables examined showed an increased titration value after heating or after acid hydrolysis. This is believed to be due to the liberation of ascorbic acid from a compound which is soluble in water, but insoluble in trichloroacetic acid. S. G. S.

Effect of Feeding Cacao Shell to Cows on the Vitamin *D* content of Butter (Milk). S. K. Kon and K. M. Henry. (*Biochem. J.*, 1935, **29**, 2051–2056.)—Cacao shell was found to contain 35 international units of vitamin *D* per g., when determined by curative and protective experiments on rats. This agrees well with the results of Knapp and Coward (ANALYST, 1934, **59**, 474), who found 28 units per g. The fat of cacao shell contains about 300 units of vitamin *D* per g. The extractable fat accounts for about 40 per cent. of the total activity of the shell. By feeding to two Shorthorn cows, under winter-stall feeding conditions, 2 lbs. of cacao shell daily for a month, the vitamin *D* content of their butter-fat was raised from the winter to the summer level, without any untoward effect on the cows. S. G. S.

Water

Determination of Lead in Potable Waters. J. F. Reith and J. de Beus. (*Z. anal. Chem.*, 1935, **103**, 13–27).—The colorimetric determination of lead as sulphide was re-investigated, the authors offering a choice of three procedures. The sample is prepared by addition of 5 ml. of 4 *N* hydrochloric acid per l. to dissolve any deposit which may contain lead. The acid is allowed to act for 15 minutes.

Procedure A, for water containing less than 10 mg. of iron per l., and either colourless or hardly coloured by organic matter: 80 ml. of prepared water are treated in a Nessler tube with 4 drops of 10 per cent. potassium cyanide solution, 10 ml. of 20 per cent. Rochelle salt, and 10 ml. of 20 per cent. ammonium chloride solution in 2 *N* ammonia, with agitation after each addition. The colour, if any, is matched against a scale of tubes containing 0, 5, 10, etc., γ of lead, and treated with the same reagents and 2 drops of fresh sodium sulphide solution (10 g. of crystals dissolved in 25 ml. of water and made up to 100 ml. with glycerin. The solution should be free from thiosulphate, *i.e.* a few ml. of 5 *N* acetic acid treated with 10 drops of the sulphide solution should show no opalescence within 15 minutes). The tube containing no lead should be practically as colourless as distilled water. The unknown solution is then treated with 2 drops of sulphide solution, and the colour is again matched against that of a scale of tubes, if necessary after a preliminary determination. The standard lead solution contains 160 mg. of pure lead nitrate and 5 ml. of 5 *N* acetic acid per l. The determination should not take more than 10 minutes, after which time bleaching takes place. The colour in terms of γ of lead prior to addition of sulphide is subtracted from the last reading.

Procedure B, for water containing more than 10 mg. of iron per l., and showing a yellow tinge due to organic matter. To 100 ml. of prepared water are added

5 ml. of 5 per cent. ammonium persulphate solution; the water is boiled down to 50 ml., cooled to 50° C., and treated with 4 drops of cyanide, and 10 ml. of Rochelle salt solution. If the liquid is clear, 10 ml. of ammoniacal ammonium chloride solution are added after a few minutes, the water is cooled, transferred to a Nessler tube, and tested as under A. If, on the other hand, the liquid is not clear, it is filtered into the tube, the filter is washed 3 times with 5-ml. portions of water faintly acidified with hydrochloric acid; the filtrate is made up to 90 ml., and treated with 10 ml. of the ammonium chloride solution; it is then tested as before.

Procedure C. This comprises enrichment by adsorption on calcium carbonate, suitable for all practical cases, including highly ferruginous water. One l. of water (or a smaller quantity of prepared water supposed to yield 50 to 100 γ of lead) is treated in a flask with 5 ml. of cyanide solution, 3 drops of phenolphthalein indicator, and just enough 4 *N* caustic soda is added, drop by drop, to faint but permanent alkaline reaction. Precipitated pure calcium carbonate (0·5 g.) is added, the water is left for an hour with occasional agitation, and decanted, after 2 to 3 hours' settling, through a small Buchner funnel. The deposit is washed 4 times with 25-ml. portions of water containing a little sodium bicarbonate, and dissolved in hot hydrochloric acid (5 ml. of 4 *N* acid and 40 ml. of water). The solution is collected in a 300-ml. flask, and, with the washings, is made up to a volume of 150 ml. The liquid is treated with 5 ml. of the persulphate solution, and boiled down to 80 ml.; hydrazine hydrochloride (0·1 g.) is then added, and boiling is continued for some minutes until the liquid is quite colourless. It is cooled and transferred (or filtered if necessary) into a Nessler tube. The blank colour of the water is now ascertained by means of a scale of 3 tubes containing 0, 5, and 10γ of lead in 90 ml. of water, 10 ml. of ammonium chloride *plus* acetate (15 and 20 per cent.) solution, and 2 drops of the sulphide reagent. The unknown water is also treated with 10 ml. of chloride-acetate reagent (which should yield a liquid neutral to Congo red, otherwise more of the reagent is required). Two drops of the sulphide solution are added, and the resultant tint is matched as before. As a check, 10 ml. of 4 *N* hydrochloric acid are added to the tube after the comparison; the colour due to lead disappears after a few minutes, whilst any due to mercury, copper or bismuth remains. W. R. S.

Agricultural

Composition of Crude Fibre. A. G. Norman. (*J. Agric. Sci.*, 1935, **25**, 529–540.)—Detailed analyses of the crude-fibre fraction from a wide range of agricultural materials showed that it consists almost entirely of cellulose and lignin, these two substances forming, on an average, 97 per cent. of the fraction. Comparison with the composition of the original material, however, indicated that the cellulose of the fibre (with the exception of bran) represented a recovery of 60 to 80 per cent., but that the proportion of lignin varied very much, and represented a recovery of 4 to 67 per cent., confirming the fact that the crude-fibre fraction does not represent any constant fraction of the plant constituents, and that the crude fibre from one material is not necessarily comparable with that from another. The composition of the fraction obtained by acid treatment indicated that this attacks the cellulose to only a limited extent, and the lignin slightly, whilst the subsequent alkali treatment appears to remove practically all the remaining hemicellulose and protein and a considerable quantity of lignin. It also largely, but not exclusively, removes the xylan of the cellulose. A discussion of the requirements of any method of assessing fibre emphasises the point that all lignin should be removed, and to achieve this the alkaline extraction must be dispensed with. Acid hydrolysis is suggested as a possible alternative empirical method, but a correction for protein would have to be introduced for all materials high in nitrogen and a determination of lignin made. D. G. H.

Organic

Determination of Free Primary and Secondary Alcohols in the presence of Tertiary Alcohols in Essential Oils by Acetylation in Pyridine. R. Delaby and S. Sabetay. (*Bull. Soc. Chim.*, 1935, **2**, 1716–1724.)—A modification of the method of Radcliffe and Chadderton (*Perf. and Essent. Oil Rec.*, 1926, **17**, 352) has been devised in which acetic anhydride is used to replace phthalic anhydride. Under the conditions described, primary alcohols, primary amines, and phenols are quantitatively acetylated in less than an hour, and secondary alcohols almost quantitatively in about an hour, whilst tertiary alcohols and aldehydes react only with difficulty. The acetylating mixture (which keeps well) is prepared by mixing 1 part by weight or volume of acetic anhydride with 2 parts of anhydrous pyridine, previously heated beneath a reflux condenser with barium hydroxide and afterwards distilled. Five ml. of the acetylating mixture are usually employed, but less may be used, the essential condition being that there must always be two or three times the theoretical amount of acetic anhydride required. Two acetylation flasks of Pyrex glass are required, each provided with a ground-in reflux condenser about 1 m. long, and one is used for a blank determination. The flasks are heated by immersion in a boiling water-bath. The initial acidity of the sample must be determined, and an allowance must be made for any ethyl alcohol present. From 0·5 to 3 g. of the substance are heated for ½ to 1 hour in the acetylating flask with 5 ml. of the acetylating mixture, 50 ml. of water are introduced through the upper end of the condenser, and heating is continued for 15 minutes, with occasional shaking. When cold, the liquid is transferred to a beaker, the flask and condenser are rinsed out with water, and the liquid is titrated with $N/2$ alcoholic potash, phenolphthalein being used as indicator. The end-point is very sharp. The following are examples of results obtained by the method, the times given being the times of acetylation:—(i) Primary alcohols: benzyl alcohol (1 hour), 99 per cent.; geraniol (½ hour), 98·7 per cent.; *l*-citronellol (½ hour), 99·3 per cent. (ii) Secondary alcohols: menthol (½ hour), 97·6 per cent.; borneol (1 hour), 95·9 per cent.; cyclohexanol (½ hour), 88·1 per cent. (1 hour), 93 and 93·6 per cent. (iii) Tertiary alcohols: methylpropylbenzyl carbinol (1 hour), nil; linalol (½ hour), 1 per cent.; terpineol (½ hour), 2·3 per cent. (iv) Aldehydes: citronellal (½ hour), 4·7 per cent.; citral (½ hour), 5·7 per cent.; (1 hour), 7·9 per cent.; benzaldehyde (1 hour), nil. (v) Primary amine: methyl anthranilate (1 hour), 99·6 per cent. (vi) Essential oil: Geranium Bourbon (acid value 3·8) (1 hour), 38·6 per cent. of geraniol. Breugnot applied the phthalic anhydride method (Radcliffe–Chadderton technique) to each of the essential oils examined by the authors and obtained results of the same order. A. O. J.

Use of Thiohydrazides as Reagents for Aldehydes. H. Wuyts and H. Wachsmuth. (*J. Pharm. Chim.*, 1935, **22**, 289–305.)—The reaction previously described (ANALYST, 1933, **58**, 481) is now applied to a number of aldehydic compounds of pharmaceutical interest, the three reagents used being α-phenyl-β-thiobenzoylhydrazine, α-*p*-bromophenyl-β-thiobenzoylhydrazine, and α-phenyl-β(thio-α-naphthoyl)-hydrazine. The compounds obtained by the condensation of these with formaldehyde, acetaldehyde, benzaldehyde, cinnamaldehyde, anisaldehyde, piperonaldehyde, dimethylaminobenzaldehyde, salicylaldehyde, vanillin and furfural are described and their melting-points given. Not only are such derivatives useful in the identification of aldehydes, but it is probable that the formation of certain of them may serve as the basis of a method of determining the aldehydes. T. H. P.

Component Fatty Acids of Glycerides of Partly Hydrogenated Rape Oil. T. P. Hilditch and H. Paul. (*J. Soc. Chem. Ind.*, 1935, **54**, 331–336T.)—Rape oil and the methyl esters prepared from its mixed fatty acids were progressively hydrogenated, and the component acids of the glycerides determined together with those of the partially hydrogenated methyl esters. Since the fatty acids of rape oil contain about equal proportions of unsaturated C_{18} (oleic and linolic) and C_{22} (erucic) acids, the ester fractionation analysis is complicated, lead erucate being only sparingly soluble in alcohol, and certain modifications of procedure are introduced. In the mixed esters hydrogenation of the linolates proceeds selectively as usual, and oleate is converted into stearate rather more readily than erucate into behenate, but in the glycerides the selectivity is less marked, owing perhaps to the configurational positions of the unsaturated radicals in combination in the glycerides. Examination of the fully-saturated glycerides produced during the progressive hydrogenation of rape oil showed no evidence of the presence of triglycerides or of trierucin. Rape oil conforms closely to the usual "even-distribution" rule characteristic of the glyceride structure of seed fats. The rape oil contained, in addition to about 6 per cent. of mixed palmito-oleo-(linoleo)-erucins, about 50 per cent. of di-C_{18}-erucin and about 44 per cent. of mono-C_{18}-dierucin (the C_{18} acid being either oleic or linolic). All possible configurations of α- and β-oleo-(linoleo)-dierucins and α and β erucodioleins (linolins) are probably present. D. G. H.

New B.S.I. Specification [for Asphaltic Compositions] and the Chemist. D. M. Wilson. (*Highways and Bridges*, 2nd Oct., 1935.)—B.S.S. No. 594 provides for the use of 3 alternative cements, *viz.*:—Asphaltic bitumen, refined lake asphalt (fluxed), and equal proportions of these. They differ widely in cost, but simple chemical analyses (*e.g.* solubility in carbon disulphide, ash-content and penetration tests) are available to show whether they meet the requirements. When, however, the asphalt cement has been manufactured into an asphalt mixture it is difficult to say for certain whether the specifications have been fulfilled, and tests are described to meet this necessity. It has been shown (*id.*, 4th Dec., 1934) that each bitumen or bitumen mixture has a characteristic colour value; the asphalt bitumens are, as a rule, darker than the bitumen in Trinidad Epuré, and the number of neutral tint units increases regularly with increasing powers of penetration. The hardening which bitumen undergoes when converted into asphalt was simulated by heating at 200° C. for a prolonged period, with and without "blowing" by a current of air, and the relationships between the penetration and colour values of the resulting products were then plotted. The curves show that in both cases (with Mexphalte and Fluxed Trinidad Epuré) the colour depends only on the degree of penetration, and is unchanged by ageing, and this conclusion was confirmed by tests on a sample from a road 9 years old. Colour values are best determined in the 0·5 cm. cell of the Lovibond Tintometer on 0·25 per cent. extracts of bitumen in benzene, the colour of solvents containing chlorine being affected by light; standard reference curves may thus be compiled for each type of bitumen. A photo-electric method is also described, in which two P.A.I. Westinghouse cells in opposition are equally illuminated by a carbon filament lamp rich in infra-red rays. One of a pair of similar cells containing benzene and a solution of the bitumen, respectively, is placed between each cell and the source of light, and the deflection of a microammeter in the cell circuit is noted; this is compared with the value obtained for the standard type of bitumen. The mineral matter in a Trinidad Epuré is an important indication of purity, because the portion passing a 200-mesh sieve contains, after ignition, approximately 19·0 per cent. of aluminium oxide. It is removed by placing the sample in a brass tube which is closed at the lower end with 200-mesh gauze and immersed in a solvent which may subsequently be removed from the extract by evaporation. The residue is ignited, silica is removed in the usual way by treatment with hydrochloric acid, and iron is separated by electrolysis of the acid solution over a mercury cathode. Aluminium may then be precipitated by means of a 2 per cent. solution of 8-hydroxyquinoline in 1·0 N acetic acid in the presence of an excess of ammonium acetate at 65° C. The usual gravimetric procedure is then followed, corrections being applied if a filler containing alumina (*e.g.* Portland cement) is present. The acid value is also a useful means of identification, and is best determined by the method used by the Royal Dutch Shell Group:—The weighed sample (5 to 7 g.) is fluxed with a suitable quantity (*e.g.* 5 ml.) of warm transformer oil or pale spindle oil of low acid value, 100 ml. of ethyl alcohol being then added and the mixture boiled under a reflux condenser for 30 minutes. It is then cooled and titrated with 0·1 N sodium hydroxide solution, with 3 ml. of a 3 per cent. solution of alkali blue 6B in alcohol as indicator, allowance being made for any blank on the reagents. Typical acid values (expressed as mg. of potassium hydroxide per 1 g. of sample) are:—Trinidad Epuré, 6·3; Panuco asphaltic bitumen, 0·5; R.O.P. asphaltic bitumen, 0·2; Triniflux, 0·8; Texaco Flux, 1·0; a mixture of Trinidad Epuré and Triniflux (80+20), 4·5. Care must be taken in interpreting results from finished asphalts, because high temperatures or mixing conditions may decrease the acid value. Therefore, although a high value denotes the presence of Trinidad Epuré, a low value does not necessarily prove that it is absent. Portland cement as a filler is often substituted partly or wholly by ragstone or limestone. The former can be detected in the fine material, separated as described above, by the presence of silica and the typical green grains of glauconite (a hydrated silicate of iron, potassium and aluminium), and the latter by a carbon dioxide determination. If Portland cement is present, the fine material gives a red colour with water and phenolphthalein. The substitution of granite by limestone, shingle or slag is detected by dissolving out the bitumen and examining the clean aggregate. Asphalt rock is specified (B.S.S. No. 596, Part 5) as the material to be used in conjunction with an asphalt cement in the manufacture of mastic asphalt, and fluorescence methods for the examination of such products are now available (*cf.* ANALYST, 1935, **60**, 493). J. G.

Determination of Mercury in Iodinated Organic Compounds. R. B. Sandin and E. T. Margolis. (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 293–294.)—Spacu's method (*Z. anal. Chem.*, 1932, **89**, 188), in which mercury is determined in presence of iodide by precipitation with a copper sulphate propylenediamine reagent, was adopted. A sample of the organic mercury compound sufficient to yield about 0·3 g. of mercury is decomposed by heating with 3 ml. of nitric acid in a sealed tube, as in the Carius method for halogen determination. The tube is opened and 20 ml. of water, 15 ml. of ammonia and sufficient potassium iodide to dissolve mercuric iodide present, are added. The liquid is diluted to 100 ml., and if free iodine is present, sodium hydroxide is added until the colour is pale yellow. The solution is heated to boiling and an excess of hot reagent [2·5 g. of copper sulphate crystals dissolved in water (amount unspecified) with 2 g. of 70 per cent. aqueous propylenediamine solution added]. After cooling for several hours in ice-water, the blue precipitate is filtered off on a weighed Gooch crucible, and washed 3 or 4 times with water containing 0·1 per cent. of potassium iodide and 0·1 per cent. of the reagent, followed by 3 or 4 2-ml. portions of 90 per cent. alcohol, and finally with 2 to 4 2-ml. portions of ether. The precipitate is dried *in vacuo* and weighed; it contains 21·81 per cent. of mercury. Good results were obtained in tests with tolylmercuric iodide and also samples of various non-iodo organic mercury compounds mixed with di-iodofluorescein. S. G. C.

Inorganic

Diphenylcarbazide as a Reagent for Hydrogen Peroxide. L. N. Lapin. (*Z. anal. Chem.*, 1935, **102**, 418–420.)—The sensitiveness of the perchromic-acid test can be increased very materially by the use of fresh diphenylcarbazide reagent, prepared by dissolving a few crystals in 0·5 ml. of 96 per cent. alcohol and adding 5 ml. of fresh absolute ether (commercial ether, which contains peroxides, cannot be used). The solution to be tested is treated with 2 to 3 drops of 20 per cent. sulphuric acid, 3 to 4 ml. of fresh absolute ether, and 2 to 3 drops of 0·01 N dichromate solution, and shaken. The ethereal layer is left to clear, and treated with 2 drops of the carbazide reagent, when a pinkish-violet tinge is given by a trace of perchromic acid not detectable by the blue colour of the ether. The limit of sensitiveness is stated to be 5γ in 5 to 10 ml. W. R. S.

Rapid and Exact Method for the Determination of Mercury. A. Augusti. (*Gazz. Chim. Ital.*, 1935, **65**, 689–693.)—When a solution of mercuric chloride or other mercuric salt is treated with an alkali chromate or dichromate and then with ammonia, the mercury is quantitatively precipitated as mercurio-ammonium chromate, $(Hg_2N)_2CrO_4, 2H_2O$. This precipitate dissolves in potassium iodide or sodium thiosulphate solution, giving $K_2(HgI_4)$ or $Na_2[Hg(S_2O_3)_2]$, together with ammonium chromate and 8 molecules of alkali hydroxide per molecule of the precipitate. Titration of the alkali yields a measure of the mercury present. A definite volume of the mercuric solution is treated, in a centrifuge tube, with a few ml. of potassium chromate or dichromate solution (either *N* or 0·1 *N*, according to the amount of mercury present) and then, drop by drop, with 10 per cent. ammonia solution until the reaction is distinctly alkaline. After some minutes the tube is centrifuged. The liquid is decanted, and the precipitate is washed several times with water, with intermediate centrifugation and decantation, and ultimately dissolved in a concentrated solution of either potassium iodide or sodium thiosulphate, and the liquid is titrated with standard oxalic acid in presence of litmus or phenolphthalein or with a mineral acid with one of the same indicators or with methyl orange: 1 ml. of 0·1 *N* acid $\equiv$ 0·01003 g. of Hg. If the mercuric salt is in the solid form, it is dissolved, in the centrifuge tube, in water or in the minimum quantity of dilute hydrochloric or nitric acid. Mercurous salts must be oxidised beforehand. T. H. P.

Colorimetric Determination of Orthophosphate in Presence of Pyro- and Metaphosphate. K. Boratynski. (*Z. anal. Chem.*, 1935, **102**, 421–428.)—Orthophosphate is the only phosphorus compound answering to the molybdenum-blue test; hence its colorimetric determination is based upon that reaction, due care being taken to depress the rate of hydrolysis of pyro- and metaphosphate. Two reducing agents were used by the author: 1.2.4-aminonaphtholsulphonic acid, and *p*-methylaminophenol sulphate, preferably the latter, as its solution is quite colourless; either reagent contained 0·5 g. of the compound in 195 ml. of 15 per cent. sodium bisulphite, and 5 ml. of 20 per cent. sodium sulphite, solution. The molybdate reagent was a 2·5 per cent. solution of ammonium molybdate in 5 *N* sulphuric acid.

The solution to be tested, diluted to 75 ml., is treated with 10 ml. of molybdate solution, and 4 of the first or 10 of the second reducing agent, and the volume is adjusted to 100 ml. The flasks should be kept for 10 minutes at 25° C. in a thermostat, then for 5 minutes at 15° C., and compared in a colorimeter with a standard (potassium dihydrogen phosphate) prepared in the same manner and at the same time. The method gave accurate results with pure orthophosphate solutions. In presence of *pyrophosphate*, it was found that the determination was correct up to a certain concentration of pyrophosphate, above which the apparent orthophosphate content progressively decreased. The irregularity was found to be related to the quantity of molybdate added, and disappeared upon addition of sufficient molybdate solution. This is explained by the observation that a yellow solution of phosphomolybdic acid is decolorised by the addition of sufficient pyrophosphate, pointing to the formation of a more stable pyrophosphoric complex which is not reduced under the above conditions. When an excess of molybdate is added, it becomes available for the formation of the reducible orthophosphate complex. The author's tests point to a molecular P_2O_5 (*pyro*): MoO_3 ratio of 1 : 6, which must be exceeded by suitable addition of molybdate reagent for the formation of the ortho-complex. *Metaphosphate* was found not to interfere, even in substantial quantities, 3 mg. of orthopentoxide being accurately determined in presence of 100 mg. of metapentoxide; 500 mg. of the latter caused a negative error of about 10 per cent. The determination in presence of *pyro- and metaphosphate* is best carried out in solutions containing not more than 0·025 g. of pentoxide (*meta*+*pyro*) in 100 ml., at which concentration the hydrolytic formation of orthophosphate from the pyrophosphate is almost negligible. W. R. S.

Detection of Potassium by means of Zinc Cobaltinitrite. J. Adams, M. Hall and W. F. Bailey. (*Ind. Eng. Chem., Anal. Ed.*, **1935, 7, 310–311.**)—Zinc cobaltinitrite precipitates potassium, and sodium may be subsequently tested for in the filtrate by the zinc uranyl acetate method. The zinc cobaltinitrite reagent may be prepared by passing a rapid stream of nitrogen oxides (made by acting on copper with nitric acid) for 45 to 60 minutes through a solution saturated with both cobalt acetate and zinc acetate; the resulting dark brown solution is stoppered and decanted from any precipitate formed after standing overnight; the reagent keeps well when tightly stoppered to prevent loss of nitrogen oxides. *Method.*—To the solution from the alkaline earth group, free from barium, arsenate, phosphate or ammonium salts, an equal volume of the reagent is added, and the mixture is kept for 15 minutes; the formation of a yellow precipitate indicates potassium. Tests of sensitiveness showed that 0·4 to 0·6 mg. of potassium per ml. was the smallest amount detectable; 1 mg. per ml. gave a precipitate immediately. Sodium in amounts up to 50 mg. per ml. was without effect. After removal of 50 mg. per ml. of potassium, 3 mg. per ml. of sodium could be detected by the zinc uranyl acetate method, or 1 mg. per ml. of sodium after the removal of 10 mg. per ml. of potassium. S. G. C.

Determination of Alkalis in Felspar. E. W. Koenig. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 314–315.)—The Berzelius method has been modified to avoid the introduction of sulphuric acid. To the sample (0·5 g., 150-mesh) is added an excess of hydrofluoric acid, and the solution is evaporated to dryness on the water-bath. The residue is extracted with water, and the whole is transferred to a 100-ml. beaker containing 2·5 g. of pure calcium oxide and boiled for 5 minutes. This precipitates iron, aluminium, magnesium and fluorine. The liquid is filtered, and the precipitated hydroxides and fluorides are washed with boiling water and discarded. The filtrate is evaporated to dryness after addition of 25 ml. of ammonium carbonate solution [200 g. of ammonium carbonate and 160 ml. of ammonia (sp.gr. 0·9) per l.]. The residue is dissolved in the minimum amount of water and digested with 15 ml. of the ammonium carbonate solution for 15 minutes; the liquid is filtered, and the residue is washed with a little cold water and rejected. The filtrate is treated with 4 drops of ammonium oxalate solution (saturated), digested hot, and evaporated to 50 ml. Any precipitate is filtered off, washed with 1 per cent. ammonium oxalate solution and rejected, and the solution is acidified with hydrochloric acid and evaporated to dryness on the water-bath. The ammonium salts are volatilised by heating at as low a temperature as possible, and the residue of alkali chlorides is dissolved in a little water, any slight precipitate being removed by filtration, and the solution evaporated to dryness in a weighed platinum dish; the salts are just melted, cooled and weighed. Results obtained with several samples of felspar were in close agreement with those furnished by the J. Lawrence Smith method. S. G. C.

Determination of Stibnite Sulphur in Ores. J. A. Tschernikhov and T. A. Uspenskaya. (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 309–310.)—The following method is proposed for the determination of sulphur, combined as antimony sulphide in stibnite and low-grade stibnite ores, containing as impurities other sulphides such as galena, copper glance, cinnabar and pyrites. It is probably applicable to mineral double sulphides such as livingstonite, boulangerite and zinkenite. The sample (200-mesh, corresponding with a maximum of 0·04 g. of sulphide sulphur) is extracted by boiling with 20 ml. of 2 *N* sodium hydroxide for 20 to 25 minutes. This dissolves out the stibnite. The liquid is filtered, and the residue of other sulphides, etc., is washed with hot 0·5 *N* sodium hydroxide solution and rejected. The solution is heated with 0·3 to 0·6 g. of aluminium foil, which precipitates the antimony and leaves the sulphur as sodium sulphide. The antimony powder is filtered off, washed with 0·5 *N* sodium hydroxide solution and rejected. To the cooled solution is added a measured excess of 0·1 *N* iodine solution (20 to 40 ml.), previously diluted to 200 ml. with water, and sufficient hydrochloric acid to neutralise the alkali and to leave about 1 to 2 per cent. of hydrochloric acid in excess. The excess iodine is back-titrated with standard thiosulphate, starch being used as indicator. Results of test experiments showed that the method is satisfactory in the presence of mineral sulphides of lead, copper, mercury and iron. Free sulphur and arsenic sulphide interfere in proportion to the amounts present, which are ordinarily slight. S. G. C.

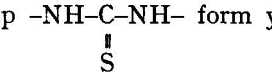
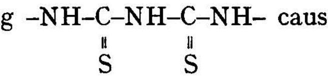
Microchemical

A Pre-heater for use in the Pregl Micro-combustion of Carbon and Hydrogen. W. F. Bruce. (*Mikrochem.*, 1935, 18, 103–105.)—A pre-heater is unnecessary when the apparatus is in constant use, but is very useful when no combustions have been made for several weeks, as it renders it unnecessary to refill the absorption tubes, and oxygen and air from any source may be used; also, larger volumes of gas than the standard amounts may be dealt with without danger of error. The pre-heater consists of a hard-glass test-tube, 1·5 × 12·5 cm., with a side-arm, and it is half-filled with wire-form copper oxide, and wrapped outside with nichrome gauze to the level of the filling. A hard-glass, 5-mm. tube is arranged to penetrate the copper gauze and reach to the bottom of the tube; the other end passes through the rubber stopper and is bent round to give a glass-to-glass contact with the arm of the bubble-counter, to which it is attached with rubber tubing. The side-arm of the test-tube is attached to the 3-way cock of the pressure-regulator of the gases. The apparatus is fixed in the horizontal position, and at the far side of the apparatus, so that it takes up no extra bench space and is not in the way. The end of the glass tube is 1 cm. higher than the stoppered end, to lessen any contact of the hot air with the rubber stopper. A tunnel of asbestos protects the micro-burner which heats the pre-heater, and an asbestos (20 × 30 cm.) shield protects the bubble-counter and rubber connections from any radiation. It is unnecessary to use aged rubber tubing with a pre-heater.

J. W. M.

Micro-volumetric Determination of Methoxyl. D. T. Gibson and T. H. Caulfield. (*J. Chem. Soc.*, 1935, 1419–1420.)—Vieböck and Schwappach (*Ber.*, 1930, **63**, 2818, 3207) have described a volumetric modification of Pregl's method which is suitable for 1 to 5 mg. of material, the alkyl iodide being absorbed in bromine, excess of which is destroyed by formic acid, the iodine then liberated on addition of potassium iodide being titrated with sodium thiosulphate solution in the presence of sulphuric acid. The sequence of reactions may be represented as follows:—$CH_3I \rightarrow CH_3IBr_2 \rightarrow IBr \rightarrow HIO_3 \rightarrow 3I_2$. The present authors find that the blank obtained from the absorbing solution is significant, being seriously increased by time, temperature, dilution and exposure to light. An amount of material corresponding with 3 to 10 ml. of 0·02 *N* sodium thiosulphate solution is desirable, and a small flame (instead of a glycerol-bath) should be used for the initial heating, which should be continued for 40 minutes after the b.p. is reached. The absorbing solution is prepared freshly by adding 6 drops of bromine to 18 ml. of 20 per cent. potassium bromide solution; half serves as a blank (the final titration of which should not exceed 0·1 ml.), and 7·5 ml. and 1·5 ml. are placed in the first and second absorption vessels, respectively, all of these solutions (including the blank) being immersed in ice-water in the same vessel. When decomposition is complete, the two absorbing solutions are washed into a conical flask with 45 ml. of 25 per cent. potassium acetate solution, and the mixture is decolorised with 1 ml. of 85 per cent. formic acid; this eliminates the error formerly considered to be due to the formation of bromates produced, owing to the presence of undissolved sodium acetate (cf. *loc. cit.*). The iodine is liberated by the addition of 2 ml. of 10 per cent. potassium iodide solution and 25 ml. of 5 *N* sulphuric acid. The maximum difference between the experimental and calculated values for organic compounds containing 5 to 34 per cent. of methoxyl was 0·47 per cent.; the error for a compound containing 62·0 per cent. of methoxyl was 1·1 per cent. J. G.

Microchemical Test for Choline and its Esters in Tissue Extracts. F. J. Booth. (*Biochem. J.*, 1935, **29**, 2064–2066.)—In dilutions of 1 in 1000 down to 1 in 50,000, choline gives a microcrystalline precipitate with Florence's reagent (potassium iodide 1·65 g., iodine 2·54 g., distilled water 30·0 g.). Albumin, glycogen and glucose in 0·5 per cent. solutions do not interfere with the sensitivity of the tests, but the influence of lipoids has not been studied. Acetylcholine does not give a crystalline precipitate, but black globules are seen. After hydrolysis with 1 per cent. sodium hydroxide solution for two minutes at room temperature, followed by acidification with hydrochloric acid to litmus, typical crystals of choline periodide were formed. The water-soluble precursor of choline, which is not precipitated by Staněk's reagent, does not react with the iodine solution until after acid hydrolysis. S. G. S.

Characteristic Atomic Groupings of Bismuth. J. V. Dubský, A. Okáč and J. Trtílek. (*Mikrochem.*, **1935, 17,** 332–343.)—A large number of organic compounds which react with bismuth salts have been investigated, and it is found that compounds containing the group  $-NH-\underset{\underset{S}{\|}}{C}-NH-$ form yellow solutions with bismuth salts, whilst the grouping  $-NH-\underset{\underset{S}{\|}}{C}-NH-\underset{\underset{S}{\|}}{C}-NH-$ causes the formation of red precipitates. For testing for bismuth the most useful compound containing the first type of grouping is thiourea, and the most useful containing the second type of grouping is mercapto-sulpho-thiobiazole (named by the authors "bismuthiole").

I. *Thiourea Test.*—The following ions do not interfere with the test:— $Pb^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Hg^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $As^{\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $NH_4^{\cdot}$, $K^{\cdot}$ and $Na^{\cdot}$. Mercuric salts, however, may be reduced on the surface of the crystal of the reagent to give a black precipitate, and always form a yellow ring round the crystals, whilst mercurous salts give a black stain, and silver salts a brown stain, and must therefore always be precipitated with dilute hydrochloric acid prior to the test. The interfering ferric ions may be reduced with sulphurous acid, and chromates with alcohol. The test is interfered with by the presence of compounds of iron and cyanogen, antimony ions, and strong oxidising agents (not, however, by NO_3' and NO_2'). Antimony salts give a light yellow stain in the conditions of the experiment, but as the reaction is less sensitive for antimony, 10γ of bismuth may be detected in the presence of 66 times the amount of antimony. *Method.*—The slightly acid test solution is tested for silver and mercury with dilute hydrochloric acid. If these elements are present they are precipitated and the test is carried out on the solution. Solutions containing ferric iron or chromate are reduced with sodium sulphite and hydrochloric acid or alcohol. Coloured solutions should be diluted so that a drop of the solution appears almost colourless. A small crystal of thiourea is placed on filter-paper, and a drop of the slightly acid test solution is placed over it. The crystal is coloured yellow at once in the presence of bismuth, and the paper is stained yellow to orange according to the amount present. *Limit of identification*: 1γ of bismuth; *concentration limit*: 1 : 30,000. A positive reaction indicates the presence of bismuth or antimony or both. For comparison, solutions of 0·1 *N* bismuth chloride and 0·1 *N* antimony chloride may be used. If small amounts of bismuth are to be detected in the presence of large amounts of antimony, the separation of the two elements in the sub-group of the hydrogen sulphide group is essential.

II. *Bismuthiole Test.*—This test is especially suitable for the identification of bismuth after its separation from the elements of the hydrogen sulphide group. The basic bismuth salt, which is filtered off in the process of separation, is washed on the filter-paper with a little ammonia and dissolved in a little dilute hydrochloric acid, and this solution is tested for bismuth. Amounts of bismuth too small to be seen on the filter-paper or in the test-tube when precipitated with ammonia, give a positive reaction in the bismuthiole test. The reagent solution is either a 1 per cent. alcoholic solution of the reagent or a solution of 0·7 g. of the reagent in 35 ml. of 0·1 *N* potassium hydroxide solution; both solutions are bright yellow. A drop of the test solution is treated with a drop of the reagent, either in a porcelain crucible or on a spot-plate, when a red to red-orange precipitate forms in the presence of bismuth. *Limit of identification*: 1·2γ of bismuth; *concentration limit*: 1 : 28,000. On filter-paper the colour appears brownish to orange and less red than on a spot-plate, and the sensitivity is less. By adding the reagent to the paper before the test solution an *identification limit* of 2γ of bismuth is attained and a *concentration limit* of 1 : 15,000. The following ions are without appreciable effect on the test:—$\mathrm{Cd}^{\cdot\cdot}$, $\mathrm{Ni}^{\cdot\cdot}$, $\mathrm{Co}^{\cdot\cdot}$, $\mathrm{Fe}^{\cdot\cdot}$, $\mathrm{Mn}^{\cdot\cdot}$, $\mathrm{Cr}^{\cdot\cdot\cdot}$, $\mathrm{Al}^{\cdot\cdot\cdot}$, $\mathrm{Zn}^{\cdot\cdot}$, $\mathrm{Mg}^{\cdot\cdot}$, $\mathrm{Ba}^{\cdot\cdot}$, $\mathrm{Sr}^{\cdot\cdot}$, $\mathrm{Ca}^{\cdot\cdot}$, and alkali ions. The following ions reduce the sensitivity:—$\mathrm{Ag}^{\cdot}$, $\mathrm{Pb}^{\cdot\cdot}$, $\mathrm{Hg_2}^{\cdot\cdot}$, $\mathrm{Hg}^{\cdot\cdot}$, $\mathrm{Cu}^{\cdot\cdot}$, $\mathrm{Sb}^{\cdot\cdot\cdot}$, $\mathrm{Sn}^{\cdot\cdot}$, $\mathrm{Fe}^{\cdot\cdot\cdot}$. Silver ions give a yellow stain on the paper, but 3γ of bismuth may be identified in the presence of 100 times the amount of silver; larger amounts of silver should be removed with hydrochloric acid. The concentration of lead ions should be reduced with hydrochloric acid, when 6γ of bismuth may be identified in the presence of 500 times the amount of lead; under similar conditions 3γ of bismuth may be identified in the presence of 240 times the amount of mercury. Copper salts should be converted into complex cyanides before the test. Antimony salts are very sensitive to the reagent, and give a yellow fleck; 20γ of bismuth, however, may be identified in the presence of 10 times the amount of antimony, owing to the formation of the precipitate in different zones on the filter-paper. In the presence of stannous ions 12γ of bismuth can be recognised in the presence of 200 times the amount of tin. J. W. M.

Cerimetric Titration of Small Amounts of Iron, with the use of αα′-Dipyridyl as an Indicator. C. J. van Nieuwenburg and H. B. Blumendal (*Mikrochem.*, 1935, **18**, 39–42.)—Standard solutions of cerium sulphate, even at concentrations of 0·002 to 0·015 *N*, are quite stable if protected from direct sunlight. *Indicator solution*: 0·25 g. αα′-dipyridyl is dissolved in 50 ml. of water, and 50 ml. of concentrated ammonia are added (this renders the end-point sharper); 5 drops of this are used for about 5 ml. of the ferrous solution. The iron is reduced to the ferrous state by the silver-reductor of Walden, Hannett and Edmonds (*J. Amer. Chem. Soc.*, 1934, **56**, 350), the acid concentration being maintained within the limits 0·5 to 1·0 *N* hydrochloric acid. The silver reductor consists of a tube, 20 cm. long and 7 mm. in diameter, with a small funnel on top and a stopcock and capillary-tube below passing into a small flask with a side-tubulure attached to a pump, by means of which the air is removed to prevent oxidation. Ferric solution of about 20 ml. volume, containing 0·1 to 10 mg. Fe, is passed through the silver reductor once, the vessel being then rinsed twice with 10 ml. of *N* hydrochloric acid and the liquid made up to a definite volume (50 ml.) and titrated with a 0·002 to 0·015 *N* solution of ceric sulphate in *N* sulphuric acid. The end-point is sharp, within one drop, and better than with a titanous solution. Results tend to be slightly low (about 0·5 per cent.), owing to oxidation by the air dissolved in the solution. Therefore for the determination of amounts less than 0·5 mg., a smaller volume and smaller reductor should be used, *viz.* a reductor 10 cm. long and 4 mm. in diameter for the determination of 0·1 to 0·3 mg. of iron in a volume of 5 ml. by means of 0·0015 N ceric solution. It is not advisable to use a sulphuric acid solution of ferrous iron, as the colour of the pyridyl complexes develops much better in hydrochloric acid. J. W. M.

Triple Nitrites of the Rare Earths and a Micro-test for Caesium. H. C. Goswami and P. B. Sarkar. (*J. Indian Chem. Soc.*, 1935, **12**, 608–610.)—The following elements of the rare-earth group were found capable of forming triple nitrites of the formula $Cs_2NaR'''(NO_2)_6$: cerium, lanthanum, praseodymium, neodymium, samarium, and gadolinium. The members of the yttrium sub-group do not yield such nitrites. The triple salts crystallise in octahedra; they are sparingly soluble, and the solutions slowly hydrolyse. For their preparation, 10 ml. of 50 per cent. rare-earth nitrate solution were treated with the same volume of 50 per cent. sodium nitrite solution; to the filtered liquid were added 10 ml. of 10 per cent. caesium nitrate solution. The yellow crystals were collected after some hours, drained and washed, first with 10 per cent. sodium nitrite solution, then with aqueous acetone, and lastly with acetone, and dried in a desiccator. The reaction is a sensitive micro-test for caesium, as rubidium and potassium do not form corresponding salts. The reagent is a filtered solution of 3 g. of praseodymium nitrate and 10 g. of sodium nitrite in 100 ml. of water, and is kept in a well-stoppered bottle. A drop of the reagent is placed on a microscope slide and touched with a loop of platinum wire dipped into the nitrate solution to be tested. After some minutes, fine octahedral crystals appear if caesium is present. A magnification ×400 is used; the sensitiveness is stated to be 0·04γ. W. R. S.

Collected References. Application of Catalysis in Micro-analysis. R. Lucas and F. Grassner. (*Mikrochem.*, 1935, **17**, 237–261.)—Catalysis is applied in qualitative tests for the following elements in certain inorganic radicals and compounds: hydrogen, sulphur, chlorine, iodine, fluorine, phosphorus, arsenic, silica, nitrogen, magnesium, copper, silver, mercury, thallium, titanium, zirconium and thorium, bismuth, vanadium, chromium, molybdenum and tungsten, manganese, iron, nickel and cobalt, and the platinum metals. These tests are briefly described and 73 references are given. Catalysis may also be applied in the following quantitative determinations: hydrogen, water, oxygen, sulphur, selenium, halogens, nitrogen, carbon, copper, silver, manganese, and certain special compounds such as urea. The methods are discussed and 70 references are given. J. W. M.

References to Microchemical Work in 1934, Part I, pp. 1-80. (Appended to *Mikrochem.*, 1935, **17**.)—A list of references to work appearing in 1934 is given in alphabetical order of the authors' names, divided into the following subject headings:—I. *Pure Microchemistry*: (i) General and apparatus, (ii) Inorganic analysis, (iii) Organic analysis, (iv) Preparative chemistry, (v) Physical chemistry. II. *Applied Microchemistry*: (i) Biological chemistry, (ii) Medical and pharmaceutical chemistry, (iii) Mineralogical chemistry, (iv) Technical chemistry. An appendix (12 pp.) contains additions to previous volumes of references appearing in 1932 and 1933. J. W. M.

Physical Methods, Apparatus, etc.

Electroscopic Method for the Detection of Yellow Phosphorus in the Presence of Tetraphosphorus Tersulphide. W. D. Treadwell and C. Beeli. (*Helv. Chim. Acta*, 1935, **18**, 1052–1060.)—The method depends on the measurement of the ionisation of air which accompanies the luminescence emitted by phosphorus during slow oxidation (*cf.* Schenk and Scherf, *Ber.*, 1906, **39**, 1522). The apparatus consists of a vertical cylindrical glass ionisation-chamber (height 14 cm., diameter 4 cm.), to the top end of which is attached the electroscope. At the base is an earthed copper nozzle placed centrally, which conducts into the cylinder, and serves as a mixer for the air saturated with water-vapour and the nitrogen which carries the phosphorus vapour, and it is essential that these do not come in contact before this point. Air is removed from the nitrogen by passing it over a layer of glowing copper filings and then, in fine bubbles, through a mixture of 1 part of 25 per cent. pyrogallol and 6 parts of 60 per cent. potassium hydroxide solutions. It then passes over a "glass-wick" immersed in a water-bath at 40° C.; this is used as a carrier for the substance to be tested, and consists of 1100 vertical glass rods, 50 mm. long and 0·5 mm. thick, which are contained in an outer glass tube. This device has been found preferable to the use of powdered zinc oxide (which is used to remove hydrogen sulphide from the phosphoric vapour before it enters the electroscope), or to pumice ground to pass a 5-mm. mesh sieve, which produces erratic results owing to irregular distribution of the phosphorus and to the effect of the acidity of the powder. The wick is easily filled by capillary action with 2 to 3 ml. of a solution of the sample in carbon disulphide, the bulk of the solvent being removed by evaporation, and the last traces by the passage of the nitrogen. The leaf of the electroscope is brought to a scale-reading of about 15 by means of rubbed sealing wax, and 55 ml. per minute of air saturated with water-vapour are passed through the ionisation-chamber, and are drawn out at the top by means of a water suction-pump. The rate of fall of the leaf (0·03 to 0·04 unit per minute) is deducted from the final value. A measured quantity of 800 ml. of nitrogen is then passed over the phosphorus in 30 seconds, the effluent gas being re-circulated several times according to the amount of phosphorus in the wick (0·1 mg. requires 2, and 0·5 to 15 mg., 4 circulations). Curves are given showing the amounts of phosphorus in terms of the sum of the rates of fall (in scale readings per minute) of the leaf for each circulation (less the blank), and they show a linear relationship for 0·1 to 1·0 mg. of P (total rates of fall 7·8 and 23·4, respectively), and subsequently a curve which is asymptotic to the blank; these enable quantitative results to be obtained. Solutions of phosphorus should be placed in a spiral wash-bottle and the nitrogen passed through at 52 ml. per minute; the method is quantitative for 20 to 60 mg. of phosphorus in 50 ml. of acetylene tetrabromide, but outside this range, or if paraffin oil is used as solvent, the method is only qualitative and is less sensitive than for samples in the solid state. Scale reading-time curves are also given for mixtures (in the solid state) containing 0 to 50 per cent. of phosphorus in the presence of tetraphosphorus tersulphide (total weight 0·2 g.), in which case the nitrogen is circulated 5 times. In all instances there is little change in the scale-reading at first, but this is followed by a very rapid change which gradually becomes slower, although, when the amount of phosphorus is small, the total change in scale-reading is also small, and an almost horizontal line is obtained. The curves show that phosphorus in the presence of the sulphide is evolved more slowly than in the pure state, and that the oxidation of the vapour of the sulphide is activated by the slow oxidation of the phosphorus, probably owing to the formation of ozone by the latter. The method is sensitive to 0·5 per cent. of phosphorus in the mixture. J. G.

Reviews

A SYSTEMATIC HANDBOOK OF VOLUMETRIC ANALYSIS. FRANCIS SUTTON. Twelfth Edition. Revised by A. D. MITCHELL, D.Sc., F.I.C. Pp. xvi + 631. London: J. & A. Churchill. 1935. Price 35s.

To open a new edition of "Sutton" may be compared with meeting an old friend after ten years' absence. We may say at once that the new edition looks very well in its new suit of print; that the old healthy spirit of criticism which distinguished the early editions is still alive, and that Time, in the person of the reviser, has dealt very kindly with our old friend.

The general arrangement remains the same. Much new matter has been added, notably a section by Dr. S. Glasstone on potentiometric titration. Many sections have been entirely re-written, and almost every page bears evidence of revision in accordance with recent improvements in methods and technique. Full use has been made of current literature, references being given to papers published in this journal as recently as 1934.

The revision has been well carried out, and the principles of selection and criticism laid down by the author in 1863 are faithfully followed. So much so, that it is difficult, even with long experience of previous editions, to detect the connecting links between the new and the old. This is as it should be.

Many reviews of previous editions have drawn attention to the freedom of this work from errata. Special mention of this feature was made in the review of the third edition, which appeared in the first volume of THE ANALYST in 1876. The present reviewer congratulates himself on having found one error, by the printer, p. 22, last line. Two of the three printer's errors in the previous edition have been corrected and the other deleted.

The reviser lays stress upon his diffidence in undertaking the task of revising a book with a tradition of seventy years behind it; the reviewer shares his feelings in writing this critique, but, with, perhaps, less regard for mere tradition, would like to offer the following thoughts for consideration.

A good start having been made at re-illustration, it is a pity that the idea was not carried further. The old wood-cuts in Part I, for instance, are hardly in keeping with the fine line-drawings that illustrate the new Part V.

In one or two places use is made of the abbreviation for "molar" as applied to a solution. A few words in explanation of the "molar," as compared with the "normal" system, seem to be called for in the introductory section—particularly in view of the popularity of this book among students. On page 14 there is a paragraph that reads as a recommendation for the use of burette-floats. The float as a means of attaining accurate readings has been superseded by carrying the calibration marks round the instrument. This paragraph requires revision or deletion. On p. 16, in the description of the method of using pipettes, the words occur: "The jet is then stroked off the side of the vessel." This is not in accordance with modern practice for instruments calibrated to N.P.L. specifications (*cf.* p. 21). On p. 25, under preservation of unstable standard solutions, mineral oil is first recommended and then stated to be useless. Space might have been saved by the simple statement that mineral oil is worthless for preventing oxidation, and by a reference to the work of Coste.

The standard temperature of calibration for volumetric apparatus and correction tables for use therewith is given as 15° C. This is, in one respect, regrettable, because it puts the twelfth edition out of date before it is fairly launched. On the other hand, it may be regarded as an advantage, in that it will allow a useful period, of say ten years, for replacement by apparatus calibrated at 20° C.; the change in capacity is negligible for most purposes.

A little more space might have been saved by deletion of methods already superseded by new ones which have been included. For example, in the standardisation of permanganate by metallic iron, paragraph (*b*), p. 120, the last sentence reads: "The content of iron in iron wire used may be determined by means of a permanganate solution that has been standardised by sodium oxalate." These words carry their own recommendation for deletion of the whole paragraph.

Those well acquainted with former editions will look for correction of points to which they may have taken exception in the past. By this test it is fairly safe to predict that they will not be disappointed with the revision. As one instance, in the preparation of standard sodium arsenite, alkali hydroxide is now decomposed by excess of acid before the addition of bicarbonate; this piece of revision was long overdue.

The specialist, turning to his own particular subject, will naturally, since it is the way of the specialist, think that he could have done it very much better himself. Let one example suffice. In the description of Lenssen's method for the determination of tin, it is stated that "the method has been almost entirely superseded by the titration with iodine in acid solution." If the word "almost" were deleted, the statement would be nearer the truth. It is in this section, dealing with applied methods of analysis—the section which has made "Sutton" so valuable in the past, and on which the book's future reputation so largely depends—that there would appear to be still room for an extension of the idea that has led to the introduction of the specially written articles on potentiometric titration and gas analysis by Dr. Glasstone and Messrs. Hollings and Thomas, respectively. There must be many, who, after long experience of some particular determination, would gladly avail themselves of an opportunity of imparting their special knowledge for the enrichment of the pages of their old friend "Sutton."

A general survey of the twelfth edition leaves the impression that the new "Sutton" is a new book. Its appearance marks a definite advance in the history of the "least perishable" of Francis Sutton's works (to quote his own words). The reviser, publisher and printer are to be congratulated on a very creditable production.

F. L. OKELL

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS. By RALPH L. SHRINER and REYNOLD C. FUSON. Pp. ix + 195. London: Chapman & Hall, Ltd. 1935. Price 11s. net.

The subject-matter of this book is presented in the form of a laboratory course for students who already have some knowledge of organic chemistry. Such laboratory courses have become increasingly popular in the last twenty-five years, and the authors fully realise their value in training the student to use his own judgment and in promoting careful observation and correct deduction.

The book is, therefore, not to be regarded as a comprehensive work. It follows lines long recognised as successful in this country, and has proved its worth in the authors' own University of Illinois.

The system described required, first of all, observation of the physical characteristics of an unknown substance, elementary analysis and determination of physical constants. Emphasis is next laid upon the examination of solubility in water, ether, inert solvents, acids and dilute alkali, whereby the substance is assigned to one group and the field of search is narrowed. "Classification tests" are then applied with specific reagents and disclose the presence of "functional groups." Likely substances are selected from lists in the book, or from general literature, and compared with the unknown. The final proof of identity comes from the preparation of derivatives.

The lists of organic substances referred to are contained in a chapter headed "The Selection of Derivatives," which occupies about half the book and includes details of the reactions and properties of about 1,600 substances. The necessity for reference to larger works, such as those of Beilstein, Richter, Mulliken and Clarke, is emphasised, and references to specific compounds dealt with in recent American literature are included.

The book closes with a chapter on the separation of mixtures, a set of problems, and a comprehensive index. The text is interspersed with exercises.

As will be seen from this description, the book follows closely the ideas behind many of the English University courses, and should, therefore, prove an acceptable alternative to similar works in use here. Special praise is due to the authors, publishers and printers for the attractive presentation and the exceptional freedom of the text from misprints. The long tables of data appear to have been equally carefully prepared.

K. A. WILLIAMS

STRUCTURE AND COMPOSITION OF FOODS. By ANDREW L. WINTON, Ph.D., and KATE BARBER WINTON, Ph.D. Volume II: VEGETABLES, LEGUMES, FRUITS. Pp. 904. New York: John Wiles & Sons, Inc.; London: Chapman & Hall, Ltd. 1935. Price 75s.

The authors in this, the second volume of the series, are concerned, as the title indicates, with fruit and vegetables. The reader, having perused it, must be left with a feeling of wonder and surprise that there is so much to say, so much to report, and so much information available regarding the botanical and chemical aspects of these classes of foods.

Part I (475 pages) deals with vegetables, with the carrot, the potato, the parsnip, no less than with the chayote, the winter squash, the velvet bean and the wrinkled pea, whilst Part II (377 pages) is concerned with fruits, well-known kinds, the pineapple, the plum and the apple, together with many which have unfamiliar names such as jack-fruit, soursop and carambola.

Each vegetable or fruit has a section to itself, and the subject-matter is divided into (*a*) a short descriptive note dealing with history and distribution, (*b*) a note on the macroscopic structure, (*c*) a more detailed comment on the microscopic structure, and finally (*d*), a summary of the chemical composition.

Most of the information on the microscopic structure is based on the original work of the authors, and the data thus presented make the book a valuable work of reference.

An extraordinary amount of facts and figures has been collected in connection with the chemical characteristics of fruit and vegetables, but it is surprising that so much of it is comparatively old (many of the references are to work reported 30 or 40 years ago). Perhaps undue emphasis is laid on this work, and not sufficient on that of more recent investigations, which have in many cases explained and often amplified the early results. For example, in the section on apples there is no reference to the influence of the "climacteric."

The number of references is extremely large (400 on a hundred pages taken at random), but there is little mention of modern English work, and few recorded analyses of English fruit. Incidentally, an amusing error is that "Carré" is referred to as "he."

From the chemical, as apart from the botanical, aspect, the volume cannot be considered seriously as a study of fruits and vegetables, and many points of loose expression of chemical facts can be found, chiefly of the type mentioned in the review of the first volume. One feels that the introduction, with a number of statements to which some exception could be taken, gives but an unfair impression of the value of the book, which is considerable. L. H. LAMPITT

TEXTBOOK OF QUANTITATIVE ANALYSIS. By W. T. HALL. Second Edition. Pp. vii + 350. London: Chapman & Hall, Ltd. 1935. Price 15s. net.

This book is adapted from Volume II (quantitative) of Treadwell and Hall's *Analytical Chemistry*. It may not be generally known that that work was originally a brief textbook written in German for students when Treadwell was teaching at Zürich. It grew in subsequent editions until it became rather a reference book than a students' textbook. In the book under review the translator has reduced the scope in order to supply the course in analytical chemistry given at the Massachusetts Institute of Technology to embryo chemical engineers.

Part I, which occupies 202 pages, represents the work given to students during the first semester. The volumetric work includes acidimetry and alkalimetry, oxidation-reduction methods with dichromate, permanganate and ceric sulphate. The theoretical aspect of these is well discussed, and the use of diphenylamine as indicator with dichromate is described. In the chapter on iodimetry one would have expected a reference to bromide-bromate solution. A chapter is devoted to precipitation methods.

The section on gravimetric analysis contains a good discussion of solubility-product and of some sources of error. A point which impresses the reviewer is the eminently practical outlook displayed in emphasising (pages 170–173) the importance of correct sampling and the references given to the literature of this subject. He doubts, however, the wisdom of encouraging students to use "factors" in chemical calculations. Practical exercises given are determinations of chlorine, iron and sulphur in simple salts, of phosphoric acid in apatite, and analyses of limestone and of Portland cement. Part I concludes with a chapter on the theory of electrolysis and the analysis of brass.

Part II covers methods which, to quote the preface, "have been developed in busy technical laboratories such as those of a steel plant." A chapter on analysis of silicates is followed by descriptions of the determination of the usual elements in steel. Some practical methods of ore analysis (other than dry assay) are dealt with, and chapters devoted to the analysis of bearing metals and to potentiometric titrations, both the hydrogen and the quinhydrone electrode being described.

It will be seen that the book is designed to cover a rather specialised course. This, no doubt, explains the absence of such features as a systematic list of methods for the determination of the leading elements and groups and their separations one from another. Likewise, gas analysis is not dealt with (though one might have expected chemical engineers to need this).

Throughout the book operations are described in considerable detail, and the underlying theoretical principles are well explained. A useful number of references to original papers (not all of them American) are given, and there is a set of problems at the end of each chapter. Some of these are unusually instructive. A student working through this book would attain a very good general grounding in analytical chemistry.

The printing and binding are good, and it is a great advantage that the book "stays put" when laid open on a bench. H. S. HOWES

WASSERSTOFF-IONENKONZENTRATION (*p*H). By H. JÖRGENSEN, with an Introduction by S. P. L. SÖRENSEN. Pp. 264. Dresden: Theodor Steinkopff. Price, 15RM. (paper); 16RM. (bound).

The realisation of the importance of hydrogen-ion concentrations, in the control of industrial processes as well as in analytical work, has resulted in the appearance of a number of important books dealing with this subject during the past decade. The present monograph differs from the others in several respects: it is not intended to be exhaustive, for the object of the book is to give a survey of the theory and application of the measurement of hydrogen-ion concentrations likely to be of particular interest to "practical" men ("praktisch-arbeitende Chemiker"). The author says, "apparatus for the determination of *p*H is to be found on expedition ships in the seas around Greenland as well as in the sugar factories of distant tropical islands"; he does not, however, attempt to cover the whole of the material between these two extremes, but has chosen sixty-two typical examples, drawn from industry and agriculture, which illustrate clearly the importance of *p*H control. References to fermentation, baking, sugar, paper, leather, organo-therapy, soil science, milk, confectionery, textiles and dyeing are included, and an attempt is made to systematise the widely differing applications according as the hydrogen-ion concentration affects the process directly, indirectly or in a complicated, hitherto unexplained, manner. Of particular interest to analytical chemists is a ten-page appendix on the significance of *p*H in acid-alkali titrations: the special value of this section lies in the fact that the author has courageously adopted the modern definition of acids and bases, as donors and acceptors of protons, respectively, with gratifying results.

The theoretical principles underlying the determination of hydrogen-ion concentrations are discussed in a brief but clear manner, and the general background of electrochemistry is described sufficiently to permit the subject to be understood by one who has been out of touch with academic chemistry for some time. The author does not aim at giving adequate practical details for determining *p*H values—in fact, the reader is referred to other treatises in this connection. Nevertheless the methods for using the hydrogen and quinhydrone electrodes are explained fully; the treatment of indicator methods and of the glass electrode is, however, not nearly so complete.

A fully indexed list of some 240 selected references completes the text of this interesting book; as the author is a Dane, the German is fortunately simple in style and quite readable. S. GLASSTONE

THE EXTRA PHARMACOPOEIA (MARTINDALE AND WESTCOTT). Vol. II. Twentieth Edition. Pp. 776 and Index 112. London: The Pharmaceutical Press and H. K. Lewis & Co., Ltd. 1935. Price 22s. 6d.

This book is so generally known as "Martindale" that its actual title seems a misnomer, and, whilst we have the British Pharmacopoeia and the British Pharmaceutical Codex as accepted books of reference, it might seem superfluous to publish an Extra Pharmacopoeia, yet it is the multitude of other things to be found in "Martindale" which has made it a necessity for medical practitioners, pharmacists, and analysts, during the past fifty years. When first published in 1883, it was a slim little volume written by a pharmacist and a doctor, and it contained information equally needed by a dispensing chemist and a busy doctor. Many a hospital dispensary possessed a "Martindale," and most doctors who drove a brougham carried the volume with them everywhere, although they seldom possessed or looked at the British Pharmacopoeia; in fact, the book might be considered the strongest link between applied medicine and chemistry. That it has remained so for fifty years is proof of its unfailing usefulness, and when the subject outgrew the space afforded by one small volume, it was arranged to publish it in two parts. After the decease of the original authors, and of the son of Martindale, who succeeded to the task of writing and publishing the book, it was considered to be such a valuable book of reference that the Council of the Pharmaceutical Society acquired the right to the copyrights, and arranged to continue the publication under the direction of an editor (C. E. Corfield) and a Revision Committee.

The volume now published is the first one to appear under the new auspices, and retains in *format* and style the familiar appearance and arrangement of its precursors. It also retains the inconvenience of finding information on a subject in the two separate volumes, and, although this is remedied in Vol. II by an index to both volumes, yet it does not make for ready co-ordination of some of the information.

It was, and still seems to be, the intention that the second volume should give information much more extensive in character than the descriptions of specific drugs and chemicals and their dosage, which are found in Vol. I, and for this reason the book may almost serve as a text-book on some subjects, among which analysis may be considered one of the most important.

Under the heading "Analytical Addenda to Chemicals and Materia Medica in Vol. II," 204 pages are devoted to substances of medical, chemical and pharmaceutical importance, whose names are comprised between Acacia and Zingiber, and a very large amount of information is condensed (perhaps collected would be a better word) in a very small space. The particulars are verified by reference to published information, and for the accuracy of these the present publishers must owe a tremendous debt to the late Dr. W. H. Martindale, and no review could attempt to criticise what must have taken a lifetime to compile and continually revise.

After this important section of the book, there are shorter ones dealing with a variety of subjects, such as:—The Action of Acids on Common Metals, Organic Reagents for Inorganic Analysis, Indicators; then some sixty pages of intensely interesting matter, *viz.*: "Scheme for the recognition of organic chemical substances used in therapeutics," the practical value of which, to almost any analyst, is incalculable, for, in addition to the scheme, the corroborative tests for some 277 substances of unusual nature are given, for which hours of search would be needed if they were sought in ordinary text-books.

The section dealing with the Chemical Tests and Microscopic Methods for the examination of Urine, Blood, Faeces and Stomach Contents, will be of special value for pathological work, and comprises all the most recent technique. For this alone the book will be in daily use in many laboratories.

The chapter on Nutrition is particularly informative, and includes the references to the most recent work and published results, and the section on Vitamins is one of the most helpful summaries of the latest information available.

Milk, Cream, Jam, Bread, and Flour, and Food Colours are all treated lucidly, and the Notes on Water Analysis are almost a treatise on that subject; so also may be described the Bacteriological and Clinical Notes, and the chapters on Sterilisation, Disinfectants, Gas Poisoning, Chemotherapy, Radium, *X*-ray Diagnosis, and Electrotherapy and Actinotherapy.

To many analysts the section on Proprietary Medicines will be of immediate interest, for, since the necessity for use of patent medicine stamps has been withdrawn, the container or label on so many of these preparations has to bear the formula or composition of the contents. The information is nowhere else presented in such an available manner, and if it is not always precise, that is no fault of the authors of the book.

Glossaries in Arabic, Danish, Dutch, French, German, Italian, Portuguese and Spanish will be helpful, and the last words "Yema de huevo" (yolk of egg) precede the Index of 112 pages, wherein is centred the vital secret of the worth of this invaluable book.

If one were asked to describe this "Martindale," it would be correct to state that it was something more than a text-book, a dictionary, a compendium, or a *vade mecum*, and to add that it embodies the life-work of two exceptional men—father and son—to which has been added the results of the Revision Committee, and the help of an editor with unique experience. C. E. SAGE

RUBBER. PHYSICAL AND CHEMICAL PROPERTIES. By T. R. DAWSON, M.Sc., F.I.C., F.I.R.I., and B. D. PORRITT, M.Sc., F.I.C., F.R.S.E., F.I.R.I. With a Foreword by Sir HERBERT WRIGHT. Pp. 700 + xi. Published by the Research Association of British Rubber Manufacturers. 1935. Price 45s.

This monumental work, produced by the co-operation of the Rubber Growers' Association and the Research Association of the British Rubber Manufacturers, may be said to form a milestone on the road of progress along which rubber technology has of late advanced very rapidly. The intention of the promoters of the book has been to provide a concise record of all the scattered data on rubber, so that not only the rubber technologist but others interested in the applications of rubber, such as engineers, architects and so on, should have such data ready to hand. The authors have not only accomplished this enormous task in a most creditable manner, but have at the same time provided the rubber industry with what it has long wanted, namely, an up-to-date survey of technical literature.

The well-known reference work of Bedford and Winkelmann (*Systematic Survey of Rubber Chemistry*) was published in 1923, whereas the present authors have utilised current literature up to March, 1934. A very large gap has thus been filled and this, in conjunction with the comprehensive subject index provided, should be of great value to the rubber technologist.

As already indicated, however, the book is not intended only for those familiar with rubber technology, but may be strongly recommended to anyone desiring information on the properties of rubber. The published price of 45s., which is very low for such an extensive work, should encourage the use of the book for this purpose.

Some idea of the contents of the book will be obtained from the following sectional headings:

It will be seen that the largest section is that dealing with the properties of soft vulcanised rubber, the applications of which include all the most important uses of rubber. The properties of latex, raw rubber, hard rubber (vulcanite) and sponge rubber are also fully covered, and conversion tables, methods of analysis and testing, specifications, list of Associations, bibliographies of the literature and authorities cited, glossary, index of mixings and subject and name index are provided.

The subject-matter is presented in tabular form with suitable explanatory headings. The scheme of arrangement of the tables, etc., follows that of the International Critical Tables, the rubber section of which is by Dr. G. S. Whitby, to whom acknowledgment is made in the foreword. Ready reference to any section of the present work can be made by consulting the comprehensive indexes provided.

The section dealing with methods of analysis and testing has been based, as far as possible, on the publications of British and foreign standardising authorities, and is a valuable feature of the book. In passing, it may be noted that no tests for traces of copper or manganese have been included, and, as these are of great importance in connection with the examination of damaged or deteriorated rubber, they might usefully find a place in this section.

A further point noted by the reviewer is the apparent absence of any data on the extreme effects of heat on raw rubber, such as, for example, the properties of "molten rubbers," destructive distillates, etc. Apart from these two points, no part of the book that the reviewer has so far consulted has been found lacking.

To conclude, this work is the most comprehensive summary of the properties of rubber ever published. It is essentially a reference book, but, as such, it should be found wherever the properties of rubber are likely to be of interest. It is hoped that its publication will materially assist in that dissemination of information on this unique substance which is so desirable for the purpose of securing its widest application.

W. H. STEVENS

Errata:

Vol. 59, 1934:

P. 828, line 12. *For* "250 ml." *read* "25 ml."

P. 801. The sentence beginning in the last line should read: "If we take, for example, a 12-stone man who has 100 p.p.m. of lead in his bones, he will have in his whole skeleton 1·5 grms. (23 grains) of lead (as Pb), or 2·9 grms. (31 grains) of lead phosphate, $Pb_3(PO_4)_2$."

Vol. 60:

P. 239, last line of Table II. *For* "6 × 6 ml. H_2O wash" *read* "6 × 10 ml. wash."

INDEX TO VOLUME 60.

INDEX TO NAMES.

INDEX TO SUBJECTS.

BRITISH ASSOCIATION
FOR THE
ADVANCEMENT OF SCIENCE

[FOUNDED 1831: INCORPORATED BY ROYAL CHARTER 1928]

CENTENARY MEETING
LONDON

September 23-30, 1931

PRESIDENT—

LT.-GEN. THE RIGHT HON. J. C. SMUTS, P.C., F.R.S.

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B (*Chemistry*)	Brig.-Gen. Sir Harold Hartley, C.B.E., F.R.S.
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K (*Botany*)	Prof. T. G. Hill.
L (*Educational Science*)	Sir Charles Grant Robertson, C.V.O.
M (*Agriculture*)	Sir John Russell, F.R.S.

The British Association seeks to promote general interest in Science and its application, and its Annual Meeting affords unique opportunity for conference and co-operation between scientific workers and others interested in all departments of Science.

The Association relies upon a full membership and attendance at its Meetings, to assure the support of the numerous scientific researches and other activities carried on under its auspices.

Particulars may be obtained on application to

THE SECRETARY, BRITISH ASSOCIATION,
BURLINGTON HOUSE, LONDON, W.1

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BRITISH ASSOCIATION
FOR THE ADVANCEMENT OF SCIENCE

Centenary Meeting, London, September 23–30, 1931

On Wednesday, September 23, 1931, at 3 p.m., the ceremony of installing Lt.-Gen. the Right Hon. J. C. Smuts as President of the Association, and a Reception of Delegates, will be held in the Albert Hall, during a private view of the Exhibition which is being arranged in connection with the Faraday Centenary Celebrations, and will be open for this occasion to Members of the British Association.

At 9 p.m., the President will deliver his Address at the Inaugural General Meeting in the Central Hall, Westminster.

The sectional and other scientific transactions will be carried on daily from Thursday, September 24, to Wednesday, September 30, inclusive. For the majority of these transactions, meeting-rooms will be used in and near Exhibition Road, South Kensington, thanks to the generous co-operation of institutions in that locality.

The Reception Room will be in the Great Hall of the University of London.

Visits to other institutions and places of scientific interest in and near London will be arranged.

A full Preliminary Programme is expected to issue in April.

As a large attendance of representative scientific workers is expected from the Dominions and foreign countries as well as from all parts of the British Isles, OFFERS OF PRIVATE HOSPITALITY by Residents in London will be gratefully received by the Association.

NO TECHNICAL QUALIFICATION IS REQUIRED FOR MEMBERSHIP. SUBSCRIPTION, £1 and upwards. (Students' tickets for duly qualified persons, 10*s.*)

TO THE BRITISH ASSOCIATION
(For address, see over)

Please forward particulars of Membership and of the Centenary Meeting to

Name..

Address..

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Date...1931.

S O January 1931. [Turn over